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Removal of Heavy Metals from Industrial Wastewaters Using Insoluble Starch Xanthate

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REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATERS USING INSOLUBLE STARCH XANTHATE

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REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATERS USING INSOLUBLE STARCH XANTHATE

by

Robert E. Wing, Leo L. Navickis,
Brian K. Jasberg, and Warren E. Rayford
Northern Regional Research Center
Agriculture Research Service
U.S. Department of Agriculture
Peoria, Illinois 61604

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Project Officer

Hugh B. Durham
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes the preparation of an agriculturally based material and its use in heavy metal cation removal from industrial wastewaters. Insoluble starch xanthate (ISX) was prepared and evaluated in wastewaters from printed circuit industries, lead battery companies, and a brass mill. Data show that ISX offers most industries having heavy metal pollution problems a material that effectively binds heavy metals and reduces their concentrations to below strict discharge limits.

The Industrial Pollution Control Division should be contacted for further information on this subject

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This report presents data that show insoluble starch xanthate (ISX) to be an effective scavenger for heavy metal ions in selected industrial effluents. Experimental procedures are presented to show the ease of preparation of ISX and its effectiveness in metal removal.

Results from bench-scale experiments utilizing ISX are given for (a) copper removal from a brass mill wastewater, (b) lead removal from lead battery effluents, and (c) copper removal from circuit board copper etchant rinse waters.

Two separate processes were developed for copper removal from electroless copper plating rinse waters and copper pyrophosphate electroplating rinse waters. Evaluations of these processes are reported.

This report was submitted in fulfillment of Interagency Agreement No. EPA-IAG-D5-0714 by Northern Regional Research Center under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 1, 1975 to June 30, 1976, and work was completed October 1, 1976.

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We acknowledge the kind assistance of Mr. John Ciancia who served as the first EPA Project Officer.

SECTION 1

INTRODUCTION

This is the final report on the Environmental Protection Agency (EPA) Project No. IAG-D5-0714 activated July 1, 1975. The purpose of this study was to develop an effective process to remove heavy metals from wastewaters of two nonferrous metal industries and one metal finishing industry with insoluble starch xanthate (ISX). More specifically, the study included the bench-scale evaluation of effluents from a brass mill, two lead battery plants and a circuit board manufacturer.

INSOLUBLE STARCH XANTHATE

It has been previously shown that water-soluble starch xanthates in combination with cationic polymers form polyelectrolyte complexes that effectively remove heavy metal cations from water (1-3). Further studies revealed that the cationic polymer could be eliminated by xanthating a highly cross-linked starch to give a water-insoluble product (4-6). This product in the sodium form, although effective in heavy metal removal, was difficult to isolate in a room temperature stable form. It has been shown (4) that ISX increased in room temperature stability if the product was converted to other salt forms. The order of stability was $Mg^{2+} >> Ca^{2+} > Na^{+} > NH_4^{+}$. A detailed description is given on how the addition of magnesium sulfate aids processing of the product and yields a product with improved room temperature stability. Data are also presented on ways to use ISX for optimum effectiveness in treatment of industrial wastewaters.

BRASS MILL WASTEWATER

Recently numerous reports (7-12) have appeared on the use of cementation with iron to remove dissolved copper from brass mill effluents. This method is effective in removing 40-60% in most cases; however, this method is not effective in reducing copper concentrations to low residual copper values.

The brass mill selected to work with is located in southwestern Illinois. Their wastewater stream enters the waste treatment facility at pH 3.5-4.0 with an average copper content of 10 mg/l and also contains zinc, nickel, and chromium (III). After neutralization, equalization and initial sedimentation, preflocculation, pH adjustment (lime trim), polyelectrolyte addition, flocculation, and final sedimentation and clarification, the wastewater is at pH 9 with a copper concentration of 0.17-0.22 mg/l (see Experimental Section for more detailed discussion). The receiving stream of their discharge is a low flow Illinois creek which provides little dilution of the treated wastewater. The Illinois Water Control Regulations require that the discharge to such a creek shall meet the General Use Water Quality Standards. The copper concentration permitted by these standards is 0.02 mg/l. A recent variance to this company by the Illinois Pollution Control Board permits a discharge copper concentration not to exceed 0.5 mg/l. All the other residual metal concentrations in the treated wastewater were below discharge standards.

Much work was done with this company to evaluate ISX in conjunction with coagulant aids while attempting to lower the copper concentration of their final effluent to 0.02 mg/l copper to meet the strict Illinois discharge limit.

LEAD BATTERY EFFLUENTS

Recently several articles were published describing lead removal from lead battery and picture tube manufacturing effluents using chemical treatment (13-19). The most common treatment technique cited for removal of dissolved lead is the reaction to form a highly insoluble lead precipitate followed by sedimentation. Because lead carbonate and lead hydroxide are very insoluble, lead is normally precipitated in these forms. The lead-containing effluents are very acidic (pH 1-2) so neutralization with lime compounds, (calcium oxide or calcium hydroxide), soda ash (sodium carbonate), or caustic soda (sodium hydroxide) is required. Each of these neutralizing chemicals has advantages and disadvantages (20).

Neutralization with Lime Compounds

The lime compounds are the lowest cost neutralizing chemicals and produce an effluent with a relatively low level of dissolved solids. Disadvantages include equipment cost and operating problems with mixing and handling the lime slurry and a potential hazard from the presence of lime dust. The main disadvantages with lime are the slower reaction rates with acids which leads to poor pH control due to lag time, and the disposal of the large volumes of lead contaminated calcium sulfate sludge. Sometimes this sludge is of suitable quality for lead reprocessing at a lead smelter.

Neutralization with Soda Ash

Soda ash costs 3 or 4 times as much as lime for an equivalent neutralizing value. There is some advantage because the equipment operation is simpler and there is less sludge that requires disposal. The use of soda ash, however, results in a high level of dissolved solids in the final discharge water. The equipment cost for mixing and dissolving the soda ash is high and the neutralization chamber must be ventilated because carbon dioxide is released.

Neutralization with Caustic Soda

Caustic soda can be purchased at a 50% wt solution strength and only a storage tank and feed pump are required for handling. The cost is 4 to 6 times that of lime for an equivalent neutralizing value. As with soda ash, there is less sludge produced but the effluent is high in dissolved solids.

After the effluent is neutralized and most of the lead precipitated, the precipitate can be flocculated with ferric sulfate or polyelectrolytes followed by sedimentation, centrifugation or filtration. For sedimentation, a lagoon with at least a 48-hr retention time is recommended, with distribution weirs for the inlet and outlet pipes. Periodic shutdown for sludge removal is sometimes required.

Current methods of battery plant wastewater neutralization were reported recently by the Illinois Institute of Technology Research Institute (21). Eight battery plants ranging in production size from 250 to 12,000 batteries per day were visited. From 42 to 290 liters of wastewater were discharged for each battery produced and the lead concentration of the effluents was 0.04-23.9 mg/1. Seven plants used hydrated lime, caustic soda, or ammonia to neutralize the effluent to between pH 7 to 8 before discharge. Some additional treatment, normally settling in lagoons, was necessary before discharging. It was concluded that the best process viewed was one that added a caustic soda solution to two cascaded stirred tanks. The first tank pH was controlled at 4.0 and the second tank at pH 8.0. The final effluent contained only 0.04 mg/1 lead; however, this process was the most expensive. The waste treatment process using hydrated lime reduced the effluent lead concentration to 0.48 mg/1 with the aid of a lagoon. Major problems of this system are disposal of lead contaminated calcium sulfate and lime precipitation in pipelines. The plant that used ammonia had the highest effluent lead concentration with 1.9 mg/1 dissolved lead and 22.0 mg/1 suspended lead. The ammonia system was the least expensive and the easiest to control; however, it was not effective in reducing the amount of dissolved lead and it added water-soluble nitrogen to the effluent.

It appears in some cases that chemical precipitation alone will reduce lead concentrations to acceptable values to satisfy present EPA limitations for discharge. The majority of companies, however, cannot meet the discharge limits. The use of other techniques will be required to satisfy the limitations on residual lead concentration and dissolved solids concentration.

Since some ion exchange materials offer an economical way to reduce pollutants from lead battery wastewaters. the use of ISX as an ion exchange material was evaluated in removing soluble lead from waters of two lead battery manufacturers. Because of the acidic nature of the effluent a neutralization pretreat was always utilized. Lime, caustic soda and soda ash were all evaluated to see if there was any difference when used in combination with ISX. The ISX was evaluated two ways, which included ISX addition to the effluent before and after filtration of the sludge.

CIRCUIT BOARD RINSE WATERS

It will be costly to develop and design effective treatment processes for the numerous different effluent streams of the printed circuit industry. Some streams will have to be segregated for special treatment, while others can be processed by conventional treatment. Counter flow rinsing, and other water use reduction methods is a start to good water management. However, the use of plating baths that contain unknown proprietary chemicals does add problems to treatment design.

Copper Removal from Electroless Copper Plating Rinse Waters

The electroless plating of copper on printed circuit boards and plastics is usually an autocatalytic formaldehyde reduction of a complexed alkaline copper (Figure 1) (22-26). For concentrated plating baths (26), treatments such as (a) raising the temperature to 50-65°C, (b) adding excess formaldehyde (1.5%) (27), (c) adding palladium activator (1-50 mg/l) (27), and (d) lowering the pH, have all been used successfully in decomposing the copper complexes. After plating is completed, it is necessary to rinse the plated articles. These rinse waters contain complexed copper which must be removed to prevent possible undesirable ecological effects as a result of introducing the copper to receiving waters or biological sewage treatment systems. These rinses with a pH around 10.9 usually contain 20-100 mg/l of copper as complexed copper. Since usual chemical treatment is not effective on these rinse waters, special treatments are required and thus involve segregation of these solutions from the main process waste waters. A simple calcium ion treatment for removing copper from some of these rinse waters is presented. A similar treatment was used by Linstrom et al. (28-30) for leaching copper oxide ores. A more universal treatment was developed using ferrous sulfate and these results are also presented.

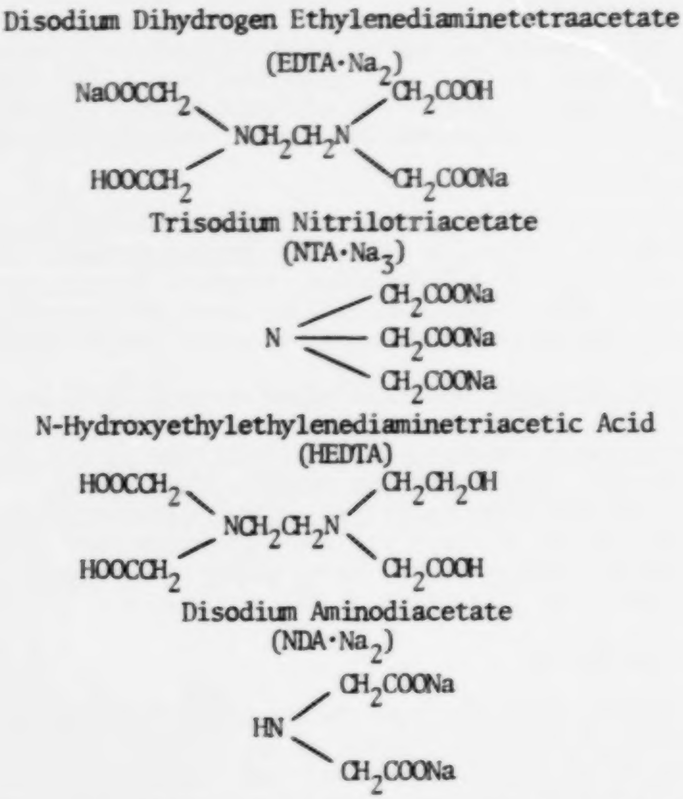
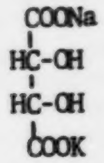

Disodium Dihydrogen Ethylenediaminetetraacetate
(EDTA·Na2)
NaOOCCH2
NCH2CH2N
CH2COOH
HOOCCH2
CH2COONa
Trisodium Nitrilotriacetate
(NTA·Na3)
N
CH2COONa
CH2COONa
CH2COONa
N-Hydroxyethylethylenediaminetriacetic Acid
(HEDTA)
HOOCCH2
NCH2CH2N
CH2CH2OH
HOOCCH2
CH2COOH
Disodium Aminodiacetate
(NDA·Na2)
HN
CH2COONa
CH2COONa

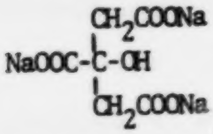
Figure 1. Structures of electroless copper complexing agents.

Sodium Potassium Tartrate

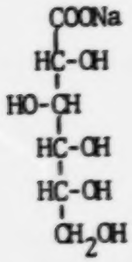
(Rochelle Salt)



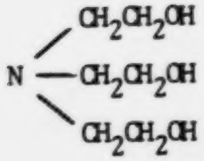
Sodium Citrate



Sodium Gluconate



Triethanol Amine



N,N,N'N' tetrakis (2-hydroxypropyl)-ethylenediamine

(Quadrol)

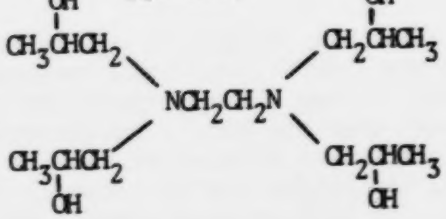


Figure 1 (continued). Structures of electroless copper complexing agents.

Copper Removal from Copper Pyrophosphate Electroplating Rinse Waters

Copper plating in alkaline media with the copper pyrophosphate complex anion has been known for over 125 years; however, it only gained commercial importance about 35 years ago (31-32). Numerous articles have appeared disclosing bath formulations, operating conditions, and applications (33-37). Most copper pyrophosphate baths utilize the components and operating conditions shown in Table 1. The predominant species in solution is the $Cu(P_2O_7)_2^{6-}$ complex which requires for its formation a weight ratio of 5.48/1 ($P_2O_7^{4-}/Cu^{2+}$). Excess pyrophosphate ($P_2O_7^{4-}$) in the bath (7.0-8.5/1) is maintained to insure complete complexation, to keep precipitates from forming, and to promote anode corrosion. Under normal operation of the bath pyrophosphate hydrolyzes according to the following equation:

$$P_2O_7^{4-} + H_2O \longrightarrow 2HPO_4^{2-}$$

TABLE 1. TYPICAL COPPER PYROPHOSPHATE BATH COMPOSITION

Constituent	g/1	oz/gal
Copper, Cu^{2+}	22-38	3-5
Pyrophosphate, $P_2O_7^{4-}$	150-250	20-33
Ammonia, NH_3	1-3	0.12-0.37
Nitrate, NO_3^-	5-10	0.67-1.33
Typical Operating Conditions		
pH	8.1-8.8	
Ratio $P_2O_7^{4-}/Cu^{2+}$	7.0-8.5/1.0	
Temperature	50-60°C	
Agitation	Air, 1-1.5 $ft^3/min \cdot ft^2$ of solution surface area	
Cathode current density	10-80 amp/ft^2	
Anode current density	20-100 amp/ft^2	
Tank voltage	2-5 volts	

This hydrolysis is increased by low pH (<8.0), high $P_2O_7^{4-}/Cu^{2+}$ ratios (>8.5/1), high temperature (>60°C), and local overheating due to insufficient agitation. The presence of some orthophosphate (HPO_4^{2-}) anion is desired for anode corrosion; however, when the HPO_4^{2-} concentration exceeds 97 to 112 g/1, the bath is usually discarded or diluted and rebuilt because the conductivity of the bath is lowered, the bright plating range is decreased, and banded deposits are obtained. The bath contains ammonia which serves to increase conductivity and to aid anode corrosion. Nitrate is present to increase the operating current density by reducing cathode polarization. Some baths contain additives, i.e., oxalate or citrate to produce some brightening and buffering action.

After the articles are plated, they are placed in a dragout or stagnant rinse tank and are subsequently subjected to a series of flowing rinses. The stagnant rinse usually is added back to the plating bath for makeup water. The flowing rinse water containing $Cu(P_2O_7)_2^{6-}$, $P_2O_7^{4-}$, and HPO_4^{2-} has to be treated before discharge to meet the ever increasingly stringent effluent guidelines. Due to the EPA regulations governing the discharge of plating effluents, treatment processes are needed to meet these limitiations. Since very little information is available on the treatment of copper pyrophosphate rinse waters (38-39), a treatment process was developed for these rinse waters.

Copper Removal from Copper Etching Rinse Waters

Ammonium persulfate and alkaline [$NH_4Cl:NH_4OH$ or $(NH_4)_2CO_3:NH_4OH$] etches are very useful in the printed circuit industry to etch copper from circuit boards. Several treatments for completely exhausted alkaline etch baths are known: (a) treatment with aluminum (40), (b) water dilution for copper carbonate precipitation (40), (c) caustic heat treatment (40-42), and (d) acid sulfide treatment (43). The "Caper"® (Continuous Ammonium Persulfate Etching and Recovery) process (44-45) is effective in keeping the etching rate high by continuously removing the dissolved copper. Rinse waters after treatment contain the $Cu(NH_3)_4^{2+}$ complex that must be removed before the rinse water can be discharged.

The treatments mentioned for the concentrated baths are not effective to lower the copper concentration consistently below 1 mg/1. A recent patent (46) describes a chemical treatment for $Cu(NH_3)_4^{2+}$ rinse waters which lowers the copper concentration to below 2 mg/1. Preliminary studies evaluating ISX on $Cu(NH_3)_4^{2+}$ rinse waters indicates it to be an effective treatment for lowering residual copper concentrations to below 0.1 mg/1.

SECTION 2

CONCLUSIONS

Insoluble starch xanthate (ISX) is an effective heavy metal ion scavenger by itself or in combination with other chemical treatments.

ISX is effective over a wide pH range (3-11) and in the presence of high salt concentrations (0-10%).

ISX is applicable to batch-type or continuous flow systems, if available engineering principles are properly applied.

ISX-metal sludge settles rapidly and dewaters to 25-50% solids after filtration or centrifugation.

Metals can be recovered from the ISX-metal sludge by a 4N nitric acid treatment or incineration.

The ISX is an inexpensive agriculturally-based product that leaves the treated effluents essentially free of heavy metal contamination, which can allow water reuse. Only sodium and magnesium ions are added to the water from an ISX treatment.

Specifically this report shows bench scale studies with ISX: (a) in combination with alum to lower residual copper levels to less than 0.02 mg/l in a brass mill wastewater without filtration, (b) to reduce residual lead concentrations to less than 0.05 mg/l in lead battery effluents without filtration, and (c) to remove copper ammonia complexes in circuit board copper etchant rinse waters.

Two treatment processes were designed to remove copper from electroless copper plating and copper pyrophosphate electroplating rinse waters.

SECTION 3

RECOMMENDATIONS

Our experiments with insoluble starch xanthate (ISX) in this report were limited to bench scale size by the scope of the project. However, the results appear sufficiently promising to warrant larger scale experiments to reinforce our laboratory findings and to realize the full potential of ISX as a scavenger for heavy metal ions.

The use of 6-in settling column, for example, in testing the brass mill wastewater with alum-ISX combinations is required to obtain copper removal and settling data before on-site evaluation using a 11 X 10^6 1/day wastewater flow.

On-site testing at lead battery companies using ISX in lead removal in batch-type and continuous flow systems is recommended.

On-site scaleup is also recommended at plating companies having uncomplexed metal rinses or copper ammonia rinses.

More information is also needed on how ISX is to be added in continuous flow operations (ISX slurry) and batch-type systems (ISX solid). The possibility of manufacturing on site is good.

We recommend also that a more extensive study be made to evaluate ISX as a filter precoat by itself or mixed with various filter aids.

SECTION 4

EXPERIMENTAL PROCEDURES

INSOLUBLE STARCH XANTHATE

General Laboratory Preparation

A highly crosslinked starch (100 g, 10% H_2O) is slurried in water (435 ml), and sodium hydroxide (45 g) in water (125 ml) is added. This mixture is stirred 30 min. Carbon disulfide (30 ml) is added and the mixture is stirred 1 hr in a covered beaker. Magnesium sulfate (19 g) in water (250 ml) is added and the mixture is allowed to stir an additional 5 min. The slurry is filtered through a Büchner funnel using Whatman No. 54 filter paper and the solid is washed with water (1,000 ml). The solid (75% H_2O) is then washed with acetone then ether. After drying for 2 hr under vacuum at room temperature, the product was analyzed. Yield 120 g; S, 9.62%; H_2O, 8.92%; ash 12.89%.

Weights of reactants and analysis of products for several preparations are found in Figure 3 and Table 3 (see pp. 25-26).

Preparations of ISX with Additional Water Washing

ISX was prepared as previously described; however, different amounts of water (1-4 l) were used during washing. The wet cake was next solvent washed with acetone then ether and then dried 4 hr under vacuum at 25°C. The products were then flash dried at 175°C and 305 m/min air velocity (1.5 sec residence time). The analysis for these products is shown in Table 4 (see p. 30).

Preparations of ISX Using Additional Magnesium Sulfate in Wash Water

ISX was prepared as previously described (General Laboratory Preparation); however, various amounts of magnesium sulfate (0-30 g) in water (500 ml) were used to wash the filtered product. The wet cakes were then washed with water (1,000 ml) and worked up as described in the previous section. The analysis of the products is shown in Table 5 (see p. 30).

Reuse of Mother Liquor in the Xanthation of Crosslinked Starch

ISX was prepared as previously described (General Laboratory Preparation); however, the first 660 ml of mother liquor and wash water was saved for subsequent xanthations. A 100-ml sample was titrated with acid (0.97N HNO_3) to pH 7.0 to determine the alkali content and make-up sodium hydroxide was added to the remaining 560 ml for the next xanthation. The products were worked up as previously described. The analysis of the products is shown in Table 6 (see p. 31).

One-Step Crosslinking and Xanthation of Starch

Commercial corn starch (100 g, 10% H_2O) is slurried in water (150 ml) containing sodium chloride (1.5 g) and epichlorohydrin (7.0 ml). To this slurry is added potassium hydroxide (6 g) in water (40 ml) slowly over 30 min and the mixture is allowed to stir for 16 hr. The suspension now containing the highly crosslinked starch can be xanthated as previously described (General Laboratory Preparation) after the addition of water (245 ml).

Pilot Plant--Rotofeed Preparation of ISX

Crosslinked starch (7.46 kg, d.b.) is slurried in water (29.84 kg) and magnesium sulfate (1.34 kg) is added. The slurry is pumped into a Baker Perkins Flowmaster Rotofeed (19.05 cm) at 890 g/min and 28°C. The sodium hydroxide (4.66N, 24 l) is metered in at 470 ml/min and the carbon disulfide (3.32 l) at 65 ml/min. The product is collected during the 50 min run and after 30 min in a holding tank, water (37.8 l) is added for easier pumping to the centrifuge. The mixture is centrifuged in a Tolhurst Centrifuge (66 cm bowl, max. 2,400 rpm) at 650 rpm and then washed with water in the machine (100 l). The cake is then dewatered to 27% solids at 1,500 rpm. The cake is flash dried and gives the following analysis: S, 9.14%; ash, 14.06%; H_2O, 3.16%.

Insoluble starch xanthate prepared commercially can be made in large reactors as previously described or it can be made continuously via a high shear mixer such as the Rotofeed, followed by centrifugation, washing, and drying. Commercially prepared products might require minor changes in reactant ratios to obtain maximum reaction efficiency.

A freeze-dried sample of the centrifuged cake gives the following analysis: S, 9.82%; ash, 14.08%; H_2O, 1.86%; Na, 10.06 mg; Mg, 8.02 mg; Na/Mg, 1.25; Capacity, 1.53 meq metal ion/g.

Flash Drying ISX

A Benco Bench Scale Vertical Pneumatic Dryer (flash drier) was used. The unit (3 m high, 3.2 kg H_2O/hr drying capacity) was run at 175°C inlet temperature and 305 m/min air velocity (1.5 sec residence time). The drier was equipped with a 2.5 cm diameter variable speed horizontal screw feeder with a vertical hopper. The wet cake of ISX (20% solids) was broken up and fed into the screw feeder. After the 3rd pass, the inlet temperature was reduced to 150°C and the air velocity to 245 m/min to minimize product decomposition. Usually a total of 6 passes were required to dry the ISX (<1% H_2O) in this small unit.

Freeze Drying ISX

A VIRTIS Company Freeze Dryer, Model FFD-42 was used. The unit has five trays with a total tray area of 1.52 m^2. The washed cake of ISX (20% solids) was slurried in water to give 5% solids (23.6 kg) and was poured into each of the five trays to a depth of 1.3 cm. The slurry froze while its temperature was reduced to -50°C. Then heat was supplied to the trays at a constant 38°C and the vacuum applied to the chamber. The vacuum was maintained at 50-100 microns during the entire drying process. About 36 hr was needed to dry this material to <1% water. The freeze drier condenser has a capacity of 22.7 kg water and 1.2 kg of ISX (<1% H_2O) was obtained.

Spray Drying ISX

A NIRO portable spray drier (Copenhagen, Denmark) with a vaned atomizer was used. The washed cake of ISX was slurried in water to give 5% solids and the slurry was fed at a rate of 3 l/hr (spindle speed, 35,000 rpm; inlet temperature, 260°C; and outlet temperature, 118°C). The recovered ISX from the cyclone contained 2-3% H_2O.

Other Drying Methods

Several other drying methods (i.e., rotary vacuum, oven tray- and drum-drying) were evaluated, all of which led to decomposition of the ISX due to the longer exposure to heat.

ISX Particle Size Distribution

The particle size distribution of a freeze-dried ISX sample was determined using a Sharples Micromerograph. The sample (0.03 g) was dispersed at the top of the 2.28 m column to break up any agglomerates and to begin settling in still air at the same moment. Figure 6 (see p. 33) shows the results of this determination.

ISX Stability Study

A flash-dried ISX sample having the following analysis (S, 11.77%; ash, 21.20%; H_2O, 0.77%; Na, 13.0 mg; Mg, 7.7 mg; capacity, 1.84 meq metal ion/g) was used to remove copper from standard copper solutions. The ISX samples were stored at 0°C and 28°C. Every two weeks 0.0278 mg of each ISX sample was added to separate beakers (50-ml samples) containing copper (31.77 mg/l) at pH 4.0. After stirring 5 min, the solutions which ranged in pH from 8.5 to 8.9 were filtered and the residual copper was measured (Figure 5, see p. 28).

Heavy Metal Removal with ISX

Synthetic solutions containing individual metal ions or mixtures of metal ions were treated with ISX by adding calculated quantities of the dry solid. The solutions were stirred for approximately 5 min at pH's 7 to 9. After filtration through Whatman 54 filter paper or medium porosity sintered glass funnels, the residual metal concentrations were determined on a Varian Techtron AA 120 spectrophotometer (Tables 8 and 9, pp. 35-36).

Copper Removal Using ISX as a Precoat on a Pressure Filter

A 3-plate stainless-steel horizontal pressure filter (Sparkler Manufacturing Company, Model 8-3) having a total filtration area of 929 cm^2 was used. The plates were covered with Sparkler filter media discs (Grade 'M', thin porous high wet-strength sheets, 21 cm in diameter with 2.5 cm center hole). A gear pump having a maximum head of 4.2 kg/sq cm at 24.6 1 per min was used to feed the filter. Two 95 1 tanks were used to supply the precoat media and copper solution. A valving arrangement was used so that the flow from either of the two tanks could be pumped without interruption to the filter. The precoat slurry [ISX (200 g) and Hi-Flow or "Super-cel" filter aid (200 g)] was suspended in water (83.3 1) and was recirculated at a rate of 11.4 1/min through the filter until the water was clear. The filter cake was approximately 1.25 cm thick and the inlet pressure was constant at 0.91 kg/cm^2. The copper solution (38.0 g $CuSO_4 \cdot 5H_2O$ in 83.3 1 of water) was passed through the cake at a rate of 4 1/min. No change in head pressure was noticed as the copper solution was recirculated through the cake. Several other runs were made varying the ratios of ISX to "Hi-flo Super-cel".

Copper Recovery from Copper-ISX Sludge

A solution (95 1) containing copper (6,000 mg Cu/1) was treated with ISX (1.89 meg metal ion/g, 100 g) by stirring for 10-12 min. After filtration and drying, the sludge (105 g) was stirred with 4N HNO_3 (500 ml) for 30 min. After filtration, the filtrate was analyzed and showed 5,994 mg Cu/1. The resulting cake was dried and analyzed (Table 17, see p. 42).

Gold-Copper Removal and Recovery from ISM Sludge

A solution (1,000 ml) containing Au (10.0 mg/1) and Cu (8.5 mg/1) was treated with ISX (0.25 g) to a final pH 7.3. The residual gold (0.204 mg/1) and copper (0.007 mg/1) were measured after filtration. The metal-ISX sludge was slurried in 4N HNO_3 (20 ml) for 30 min, filtered, and water washed and the filtrate diluted to 1 1. Metal analysis of the filtrate gave gold (0.000 mg/1) and copper (8.6 mg/1). The sludge was then slurried in aqua regia (20 ml) for 5 min, filtered, water washed, and the filtrate diluted to 1 1. Metal analysis of the filtrate gave gold (9.8 mg/1) and copper (0.000 mg/1).

BRASS MILL WASTEWATER

Equipment

Phipps-Bird six position ganged stirrer with voltage regulator.
Lourdes Beta-Fuge A2 centrifuge.
Sharples Super Centrifuge; 10.5 cm diameter bowl.

Sharples Super Decanter P-600.
Gear Pump (24.6 l/min max) with rotameter.
Feed tank with with cone bottom (150 l) with air driven stirrer.

Materials

Inorganics Evaluated--

Powdered calcium hydroxide [$Ca(OH)_2$; reagent grade] added as a solid.
Ferrous chloride ($FeCl_2$, reagent grade) added as a 0.5 g/l solution.
Ferric chloride ($FeCl_3$, reagent grade) added as a 0.5 g/l solution.
Aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$ (alum), reagent grade] added as a solid.
Sodium sulfide (Na_2S, reagent grade) added as a 0.5 g/l solution.
Sodium hydroxide (NaOH, 0.12N).
Hydrochloric acid (HCl, 5 wt %).
Bentonite (clay) added as a solid.

Polymers Evaluated--

Insoluble-starch xanthate (ISX, 1.5 meq metal ion/g) was prepared as previously discussed and was added as a solid.

Soluble starch xanthate (SSX) was evaluated as an anionic flocculant and was prepared as follows:

Commercial corn starch (324 g, 10.0% H_2O) is slurried with an axial flow impeller in water (2,400 ml), and sodium hydroxide (40 g) in water (200 ml) is added. This mixture is stirred 30 min. Carbon disulfide (24.3 ml) is added and the mixture is stirred rapidly for 1 hr in a covered beaker. The mixture ($\sim$10% solids, degree of substitution = 0.11) is stored at 5°C and freshly diluted 5.07 g/l for use.

Olin 5002 (Olin Corp.) added as a 0.5 g/l freshly prepared solution.

Dearborn 420 (Dearborn Chemical Company) added as a 0.5 g/l freshly prepared solution.

Nalcolyte 676 (Nalco Chemical Company) added as a 0.5 g/l freshly prepared solution.

Analysis

Copper--

The initial and residual copper concentrations in unfiltered acidified samples were determined on a Varian Techtron AA 120 Spectrophotometer.

Turbidity--

The clarity (or turbidity) was judged by visual observation.

Brass mill wastewater

Samples were taken by treatment facility operators as the wastewater leaves a 15-ft deep continuous flow clarifier, usually before chlorination. The clear, pale yellow samples containing a few suspended solids were 24-36 hr old when received. The pH range and total copper content of different 19 l plastic containers were 8.6-9.5 and 0.088-0.210 mg/l, respectively. The containers were vigorously shaken before being sampled.

Present On-Site Treatment--

This brass mill is presently treating an average of 11 X 10^6 l/day but can accommodate up to 17.4 X 10^6 l/day during rainfall (Figure 2).

Neutralization--The wastewaters received at the facility are acidic and require neutralization to minimize corrosion of the treatment plant elements, to enhance the effectiveness of the overall treatment process and to meet state water quality criteria. Neutralization is accomplished by the addition of a 2.5% w/v solution of lime during vigorous mixing by turbine agitators, until the pH of the wastewaters reach a predetermined value (pH 5.5 to 6).

Equalization and initial sedimentation--Following neutralization, the wastewater flows by gravity into the equalization-sedimentation system. This system accomplishes equalization by hydraulically controlling and attenuating hydraulic surges and contaminant peak concentrations and provides for the removal by sedimentation (settling) of a high percentage of settleable solids material in the wastewaters. The settling of solids from the wastewaters (~6 hr hold time) is accomplished through gravitational forces. The settled materials are pumped to the sludge thickening unit for further treatment. This basin is also equipped with mechanical surface skimming devices which continuously remove scum and floating debris from the wastewaters before they are passed to subsequent units. The basin is also equipped with magnetic flow meters and control valves to provide hydraulic flow control. Emergency overflow from this basin to an emergency holding lagoon is provided.

Pre-flocculation, pH adjustment ("lime trim")--This unit process is an extension of the initial neutralization to insure pH control which is vital to completing the precipitation of heavy metals and other contaminants by chemical flocculation and coagulation. The optimum pH range for the "lime trim" system is between pH 8 and pH 9, but the operating range is between pH 8 and pH 10.

Polyelectrolyte addition--In the "lime trim" system, the heavy metals are converted to hydroxide forms, and exist as finely divided colloids. Anionic polyelectrolytes (1.4 mg/l) cause these fine particles of metal hydroxides to agglomerate in preparation for removal by flocculation and sedimentation.

Flocculation and final sedimentation--These unit processes occur in a single basin designed to accomplish these two functions simultaneously. Flocculation is an extension of the agglomeration process initiated by the addition of the anionic polyelectrolyte. Mechanisms in the flocculator

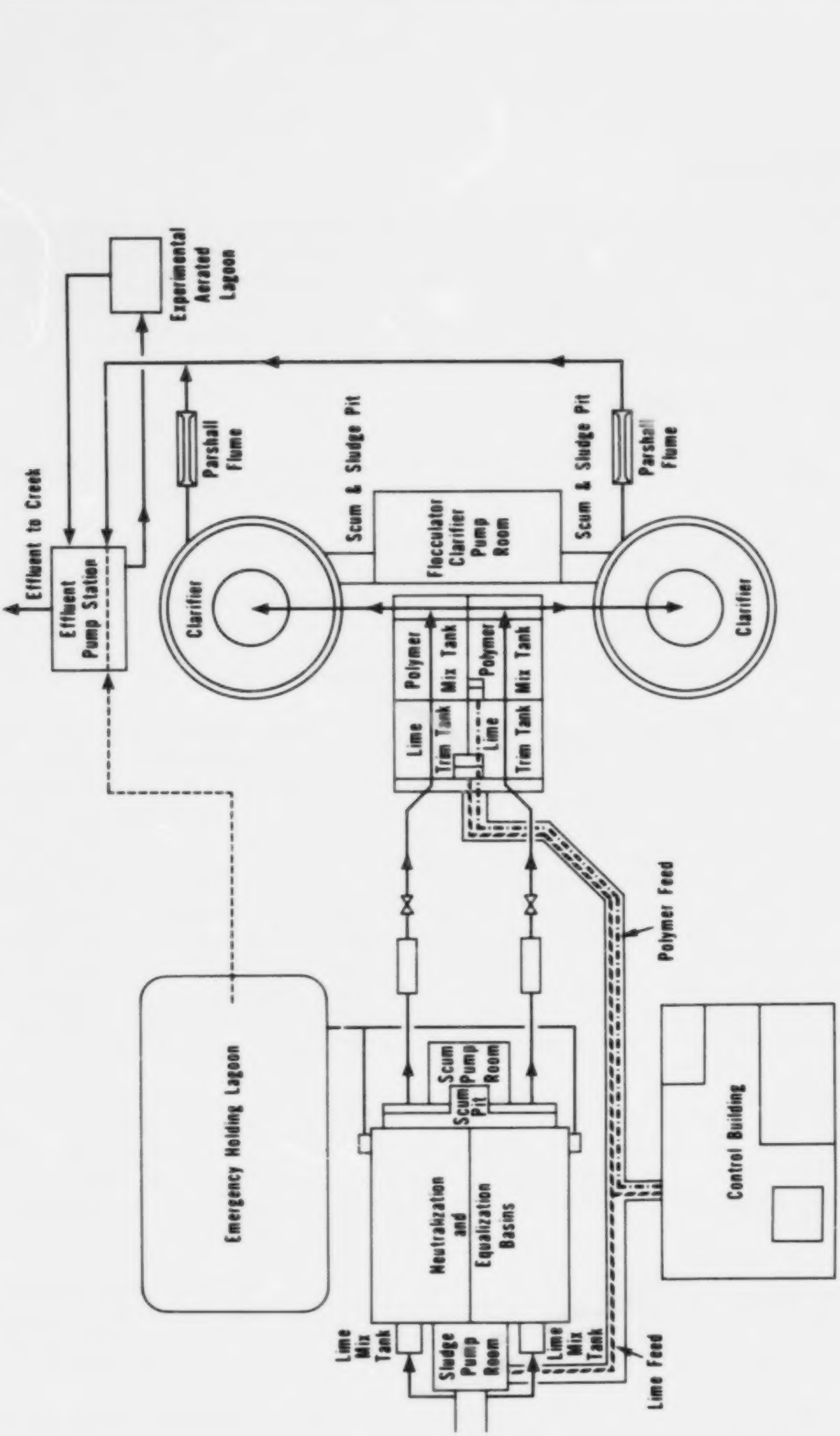

Effluent to Creek
Effluent Pump Station
Experimental Aerated Lagoon
Parshall Flume
Scum & Sludge Pit
Parshall Flume
Scum & Sludge Pit
Clarifier
Flocculator Clarifier Pump Room
Clarifier
Polymer
Mix Tank
Polymer
Mix Tank
Lime
Trim Tank
Lime
Trim Tank
Polymer Feed
Emergency Holding Lagoon
Scum Pump Room
Scum Pit
Neutralization and Equalization Basins
Control Building
Lime Mix Tank
Sludge Pump Room
Lime Mix Tank
Lime Feed

Figure 2. Brass mill treatment facility.

oscillate at a predetermined slow rate thus causing the agglomerated particles to collide and increase in size. As these particles grow in size they enter the sedimentation portion of the basin where they settle out.

Wastewaters at this stage have been separated into two fractions, a clear supernatant and settled sludge. The clarified supernatant represents the treated effluent to be discharged to a creek through a measuring device (Parshall-flume) and is practically free of all dissolved metals and solids. The settled sludge contains the heavy metals, lime, and other contaminants removed by chemical coagulation.

Flocculator clarifier basins are equipped with surface skimmers to remove floating material. This floating material is discharged to the sludge well and mixed with the sludge. The sludge and scum (∿5% solids) are now ready to be transferred to the sludge thickening unit.

Experimental lagoon--An experimental lagoon is available for tests to provide additional data to the brass mill on the removal of soluble organic material from the chemically treated effluent. This data will be available for future design purposes should water quality criteria change drastically to require further removal of soluble organic materials from the brass mill effluent.

Emergency lagoon--An earthen lagoon acts as a surge tank for peak hydraulic flows due to storms. This lagoon is sealed with an asphaltic liner and is equipped with an emergency overflow to the outfall facilities.

"Synthetic" Copper Solutions

For comparative jar testing, "synthetic" copper samples were prepared (∿0.20 mg/l) by dissolving $CuSO_4 \cdot 5H_2O$ in distilled water. The pH was raised to the test value with calcium hydroxide. Any slight flucculations in pH were controlled with dilute sodium hydroxide or hydrochloric acid.

Standard Jar Test Method

Samples (brass mill or synthetic copper, 950 ml) were placed in six 1-l beakers, which were placed on squares of insulation material to minimize convection currents. The paddles were lowered into the samples and the samples were stirred at 100 rpm. The pH of all the samples was adjusted to the test value (usually 9.0) with calcium hydroxide and samples (10 ml) were taken for "initial copper." ISX was added and after 10 min the other additives were added where desired. The pH was usually readjusted to the test value. The stir speed was then decreased to 50 rpm for 5 min and then to 20 rpm for 60 min. Some tests were only stirred for 12 min as noted. During the 20-rpm stir, the time for floc appearance was noted. The pH was constantly maintained at the desired value during the slow stir period. The pH of the brass mill wastewater remained fairly constant apparently due to some buffer capacity, whereas the pH of the synthetic samples tended to decrease probably due to carbon dioxide absorption and no buffering.

At the end of the 60-min (or 12-min) stir, the paddles were removed to allow unhindered settling. During the settling, the beakers were observed for settling rate and clarity. After 10 and 30 min, samples (10 ml) were withdrawn by pipette or by a manifold sampling arrangement at a point in the center of the beaker 3.2 cm below the surface. Care was taken to avoid any floating solids. The withdrawn samples were acidified, without filtering, with two drops of copper-free concentrated hydrochloric acid and the copper concentration determined by AA. A standard curve (0.01-0.50 mg/l copper) was made each day with 0.01 mg/l copper as the lower limit of measurement.

Batch Centrifuging Test Method

Brass mill samples (1,000 ml) were sampled for initial copper and ISX (28 mg) was added. After stirring (30 min), aliquots (20 ml) were placed in centrifuge tubes. They were spun in the Beta-fuge for the times and speeds shown in Figure 11 (see p. 49). The temperature was maintained at 24 ± 2°C by refrigeration. On all runs, the times shown were taken when the speed was reached and then the brake was applied. At the end of each run, aliquots (10 ml) were taken from the tubes and analyzed for total copper after acidification (2 drops of concentrated HCl). The results are shown as residual copper vs spin time (min) at the G's shown (Figure 11, Table 19).

Continuous Centrifuging Test Method

Brass mill samples or synthetic copper solutions were placed in the feed tank where the pH was adjusted, and ISX or sulfide added. After a rapid stir for 10-15 min, an aliquot (20 ml) was removed for copper analysis. Coagulant aids (alum or polymers) were added where desired and the pH readjusted where desired. After a slow stir (4-5 min) an aliquot (20 ml) was taken for initial copper analysis. The slurry was pumped into the rotating "Super-Centrifuge" bowl. Samples of the centrate were collected, acidified without filtering and analyzed for total copper. The conditions of these runs and results are shown in Tables 18 and 20 (see pp. 48, 51).

The same procedure was used with the P-600 Super-Decanter. This machine has a scroll discharge which conveys the solids from the bowl. Since only small quantities of sludge were formed by our treatments, the scroll was disconnected and rotated with the bowl, so there was, presumably, no disturbance of the settled solids. In actual use, the scroll might resuspend some of the finer particles (Table 20, see p. 51).

LEAD-BATTERY EFFLUENTS

Materials

Neutralization Agents Evaluated--

Sodium hydroxide (NaOH) was added as a 7N solution (280 g/l).
Sodium carbonate (Na_2CO_3) was added as a 10% solution (100 g/l).
Calcium hydroxide [$Ca(OH)_2$] was added as a solid.
Calcium carbonate ($CaCO_3$) was added as a solid.

Polymers Evaluated--

Insoluble starch xanthate (ISX, 1.5 meq metal ion/g) was prepared as previously discussed and was added as a solid.

Soluble starch xanthate (SSX) was evaluated as an anionic flocculant and was prepared as previously described.

Commercial anionic polymers (0.5 g/1)--

Dow A-23 (Dow Chemical Company).

Magnifloc 837A (American Cyanamid Company).

Nalcolyte 676 (Nalco Chemical Company).

Analysis

Metals--

Lead and iron concentrations were determined on a Varian Techtron AA 120 spectrophotometer.

Suspended Solids--

Determined by filtration of 1-1 solutions through fine porosity predried sintered glass funnels and redrying at 110°C.

Dissolved Solids--

Determined by evaporation of 1-1 solutions to dryness, and then drying flasks at 110°C for an hour.

Lead Battery Effluent Sample (Indiana)

The sample (40 1) stored as received gave the following analysis: total lead (4.05 mg/1), total iron (52.0 mg/1), pH (1.6), suspended solids (39.3 mg/1), and dissolved solids (4.94 g/1).

Present On-Site Treatment (Indiana)

This company presently treats their raw wastewater (75,700 1/day, 100 mg/1 total lead) by first settling the suspended lead to lower the lead concentration to 5-20 mg/1. This is followed by adjusting the pH to 7.0 with soda ash and allowing the sludge to settle for 2-7 days in tanks. They have evaluated on-site sodium borohydride-coke, peat and ISX to lower their lead concentration to 0.05 mg/1 with some success. The company would like to go to complete water recycle; however, their present dissolved solids concentration is too high. They have considered passing their wastewater after settling through a sand filter, charcoal filter, reverse osmosis unit, and a final deionizer.

Lead Battery Effluent Sample (Pennsylvania)

The sample (40 1) was stored as received and gave the following analysis: total lead (1.03 mg/1) and pH (10.6).

Present On-Site Treatment (Pennsylvania)

This company presently treats 570,000-950,000 1/day (initial pH 1.0) with hydrated lime to pH 6.0-9.0. After anionic polyelectrolyte addition, the sludge is settled in clarifiers and settling basins. They have to lower their total lead to 0.05 mg/1 and dissolved solids to 500 mg/1. Their suspended solids concentration is presently below discharge limits.

Preliminary Experiments

Preliminary studies were conducted on the Indiana lead battery wastewater to determine: (a) effectiveness of sodium hydroxide, sodium carbonate, calcium hydroxide, and calcium carbonate as neutralization agents in metal removal, floc settlability, and dissolved solids reduction, (b) effectiveness of ISX for lead removal, (c) effectiveness of soluble starch xanthate for lead removal and flocculating ability, (d) effectiveness of commercial anionic polymers in flocculating ability, and (e) effectiveness of barium carbonate in dissolved solids reduction.

Results of these studies are shown in Tables 26-29 (see pp. 64-67).

Standard Jar Tests

These tests were conducted using the preliminary testing data as a guideline. Results of these studies are found in Tables 30-31 (see pp. 68-69).

CIRCUIT BOARD RINSE WATERS

Copper Removal from Electroless Copper Plating Rinse Waters

Stock Copper Complex Baths--

Commercial baths were used as received or were prepared according to supplier data sheets. Synthetic baths (51) were prepared as described in Table 2.

Calcium Treatment of Rinse Solutions--

In most cases 1-1 solutions of 5-100 mg/1 copper in complex form were treated at room temperature with either calcium hydroxide, calcium oxide, calcium chloride, or calcium sulfate to pH 11.5-12.0 to precipitate the copper as its hydroxide. The suspended copper hydroxide after a 5-min stirring time was flocculated with 1.5 mg/1 anionic polyelectrolyte solutions (i.e., 0.5 g/1 solutions of either Nalcolyte 676 or Dow Purifloc A-23). After separation via filtration through Whatman 54 filter paper, the residual copper was measured via atomic absorption with a Varian Techtron AA 120 spectrophotometer.

TABLE 2. SYNTHETIC ELECTROLESS COPPER BATH COMPOSITIONS (51)

Bath	Components	Molecular weight	Solution Conc.		Copper Conc., mg/l
			moles/l	g/l	
EDTA*	$CuSO_4\cdot5H_2O$	249.69	0.030	7.49	1,910
	NaCN	49.01	0.0004	0.0198	
	NaOH	39.99	0.125	5.00	
	Formaldehyde (37%)	30.03	0.08	6.5 ml	
	$EDTA\cdot Na_2\cdot2H_2O$	372.25	0.036	13.40	
NTA†	$NTA\cdot Na_3\cdot H_2O$	275.00	0.0425	11.69	1,730
HEDTA†-‡	HEDTA	278.26	0.036	10.02	1,890
NDA†	$NDA\cdot Na_2$	195.08	0.10	19.50	1,790
Tartrate§	$CuSO_4\cdot5H_2O$	249.69	0.020	5.00	1,082
	NaCN	49.01	0.0002	0.0099	
	NaOH	39.99	0.125	5.00	
	Formaldehyde (37%)	30.33	0.47	38.1 ml	
	Tartrate·Na·K	282.25	0.0425	12.00	
Citrate§	$CuSO_4\cdot5H_2O$	249.69	0.02	5.00	1,122
	NaCN	49.01	0.0002	0.0099	
	NaOH	39.99	0.125	5.00	
	Formaldehyde (37%)	30.33	0.40	32.43 ml	
	$Citrate\cdot Na_3\cdot2H_2O$	294.11	0.051	15.00	
Gluconate#	Gluconate·Na	218.16	0.05	10.90	1,551
Triethanol amine#	$N(CH_2CH_2OH)_3$	149.00	0.05	7.60	1,120
Quadrol#	Quadrol	292.00	0.026	7.60	1,282

* All reagents were dissolved individually in water. The copper solution was added to the EDTA solution. The sodium cyanide was added to the sodium hydroxide solution. This mixture was then added to the complexed copper and the volume adjusted to 1 l.

† All constituents and amounts as described in (*) were the same except for the complexing agent.

‡ The HEDTA solution was adjusted to pH 7 with sodium hydroxide before addition of the copper solution.

§ Follow EDTA procedure (*).

# Use citrate bath concentrations and follow (*).

Ferrous Sulfate Treatment of Rinse Solutions--

Solutions (1,000 ml) of 10-50 mg/1 copper in complex form were acidified to pH 2.7-5.0 with 1N H_2SO_4 and ferrous sulfate (0.2-1.0 g) was added. After stirring (5-60 min) the solutions were adjusted to a pH greater than 11.0 with calcium hydroxide or sodium hydroxide and the precipitate was flocculated with anionic polyelectrolyte (2.5-5.0 mg/1). After filtration, the residual copper and iron concentrations were measured (see pp. 89-92, Tables 47-50).

Copper Removal from Copper Pyrophosphate Electroplating Rinse Waters

Rinse Waters--

Synthetic rinses were prepared according to supplier data sheets. Industrial rinses were used as received.

Treatment of Rinse Waters--

Solutions (500 or 1,000 ml) containing various amounts of copper, pyrophosphate, and orthophosphate were treated with various combinations of calcium hydroxide or calcium chloride and calcium hydroxide to a pH greater than 9. After flocculation of the precipitate with an anionic polyelectrolyte, the solution was filtered and the residual copper and phorphorus concentrations were determined (see p.96, Tables 54-55).

Copper Removal from Copper Etching Rinse Waters

Solutions (1,000 ml) containing various concentrations of $Cu(NH_3)_4^{2+}$ from synthetic and actual industrial rinses were treated with various amounts of ISX. Residual copper concentrations were measured after a 5-min ISX contact time followed by filtration (see p. 100, Figure 20).

SECTION 5

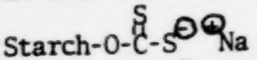
RESULTS AND DISCUSSION

INSOLUBLE STARCH XANTHATE

Even though the main purpose of this project was to evaluate ISX for heavy metal removal, a considerable amount of time was spent developing a way to stabilize ISX to some degree so that its metal scavenging usefulness could be utilized for industrial pollution control. The addition of magnesium sulfate during the preparation of ISX, gives this added stability, so the product can be manufactured and have a reasonable shelf life before any degradation occurs. The magnesium sulfate addition also affords (a) increased filtration or centrifugation rates during workup, (b) increased flash drying feed rate, and (c) increased settling rate in heavy metal cation removal.

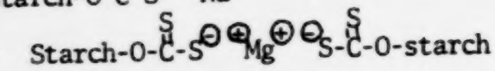
The structure of ISX described in this report is a combination of the sodium- and magnesium-form as shown below. When ISX removes heavy metals

Sodium form:



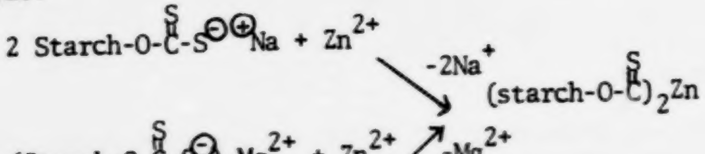
$$\text{Starch-O-}\overset{\underset{\|}{S}}{C}\text{-S}^{\ominus}\,{}^{\oplus}\text{Na}$$

Magnesium form:



$$\text{Starch-O-}\overset{\underset{\|}{S}}{C}\text{-S}^{\ominus}\,{}^{\oplus}\text{Mg}^{\oplus}\,{}^{\ominus}\text{S-}\overset{\underset{\|}{S}}{C}\text{-O-starch}$$

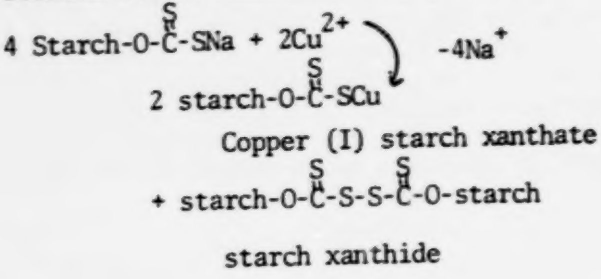
from the solution, the usual mechanism of removal is shown using zinc as an example.



$$2\ \text{Starch-O-}\overset{\underset{\|}{S}}{C}\text{-S}^{\ominus}\,{}^{\oplus}\text{Na} + \text{Zn}^{2+} \xrightarrow{-2\text{Na}^{+}} (\text{starch-O-}\overset{\underset{\|}{S}}{C})_2\text{Zn}$$

$$(\text{Starch-O-}\overset{\underset{\|}{S}}{C}\text{-S}^{\ominus})_2\text{Mg}^{2+} + \text{Zn}^{2+} \xrightarrow{-\text{Mg}^{2+}} (\text{starch-O-}\overset{\underset{\|}{S}}{C})_2\text{Zn}$$

However, when ISX removes copper (II) from solution, an oxidation-reduction takes place as illustrated below. This mechanism has been shown previously with soluble starch xanthates and alcohol xanthates (47-49).



$$4\ \text{Starch-O-}\overset{\underset{\|}{S}}{C}\text{-SNa} + 2\text{Cu}^{2+} \xrightarrow{-4\text{Na}^{+}} 2\ \text{starch-O-}\overset{\underset{\|}{S}}{C}\text{-SCu}$$

Copper (I) starch xanthate

$$+\ \text{starch-O-}\overset{\underset{\|}{S}}{C}\text{-S-S-}\overset{\underset{\|}{S}}{C}\text{-O-starch}$$

starch xanthide

Several preparations of ISX were made to evaluate reactant ratio effects and the amount of magnesium sulfate required for product optimization (Figure 3 and Table 3). Figure 3 shows the %S incorporated in the product for different volumes of carbon disulfide. Under the reaction conditions used, 30 ml of carbon disulfide would yield a product containing the most sulfur. Due to the volatility of carbon disulfide a closed or covered reactor is necessary for maximum xanthate formation. If carbon disulfide is used according to manufacturer's brochures, it can be safely handled.

A preliminary study was made under constant reaction conditions (CS_2, 15 ml) to determine the optimum amount of magnesium ion required to give the most rapid dewatering rate of the product when filtered. Figure 4 shows the inverse crack time required for the reaction slurry to be dewatered (product cake to crack) vs the weight of magnesium ion used in the preparation which would yield a product containing 5-6% sulfur. This means that for each % S in the final product, 0.4 g magnesium ion (2.0 g $MgSO_4$) should be added for maximum filtration rate. Analysis of the filtrate showed all the magnesium to be incorporated into the product. Magnesium chloride was also evaluated with equal effectiveness in product workup, however, proportionately larger amounts of a more expensive chemical would be required.

The addition of the magnesium sulfate solution caused the reaction slurry to thicken initially; however, after 60 sec, the slurry became thin and was easily filtered. The magnesium sulfate can also be added at the beginning of the xanthation or added throughout the xanthation yielding equally effective products.

Previously (4-6) it was shown that ISX in the sodium form was very stable at 0°C; however, it only had a limited room temperature stability (1-2 days). Treatment of the dry sodium form with physical mixtures of magnesium oxide or magnesium sulfate showed no improvement in stability. The magnesium ion treatment just described gives a product that is more stable at room temperature which would allow the preparation, shipment, and use before partial degradation occurred. If the product is stored below 10°C, the stability increases significantly (2 mo) and at 0°C very little change is observed after 1-yr storage.

The stability of ISX was determined by evaluating copper removal over a period of 10 weeks with ISX samples stored at 0° and 28°C. Figure 5 shows that the product stored at room temperature decomposes after 6 weeks, whereas the product stored at 0° is still very effective in copper removal. Some decomposition was noted after two weeks with the room temperature product as the color started changing (pale yellow to gold) and slight color development was noted when the sample was added to the copper solution; however, the copper removal was good since the copper-ISX decomposition products precipitated at a pH>8.5. After eight weeks, the product decomposed to such a degree that the copper-decomposition products remained in solution (amber color) and resulted in high residual copper values. The color and residual copper, however, can be completely removed by adding a small amount of 30% hydrogen peroxide above pH 8.

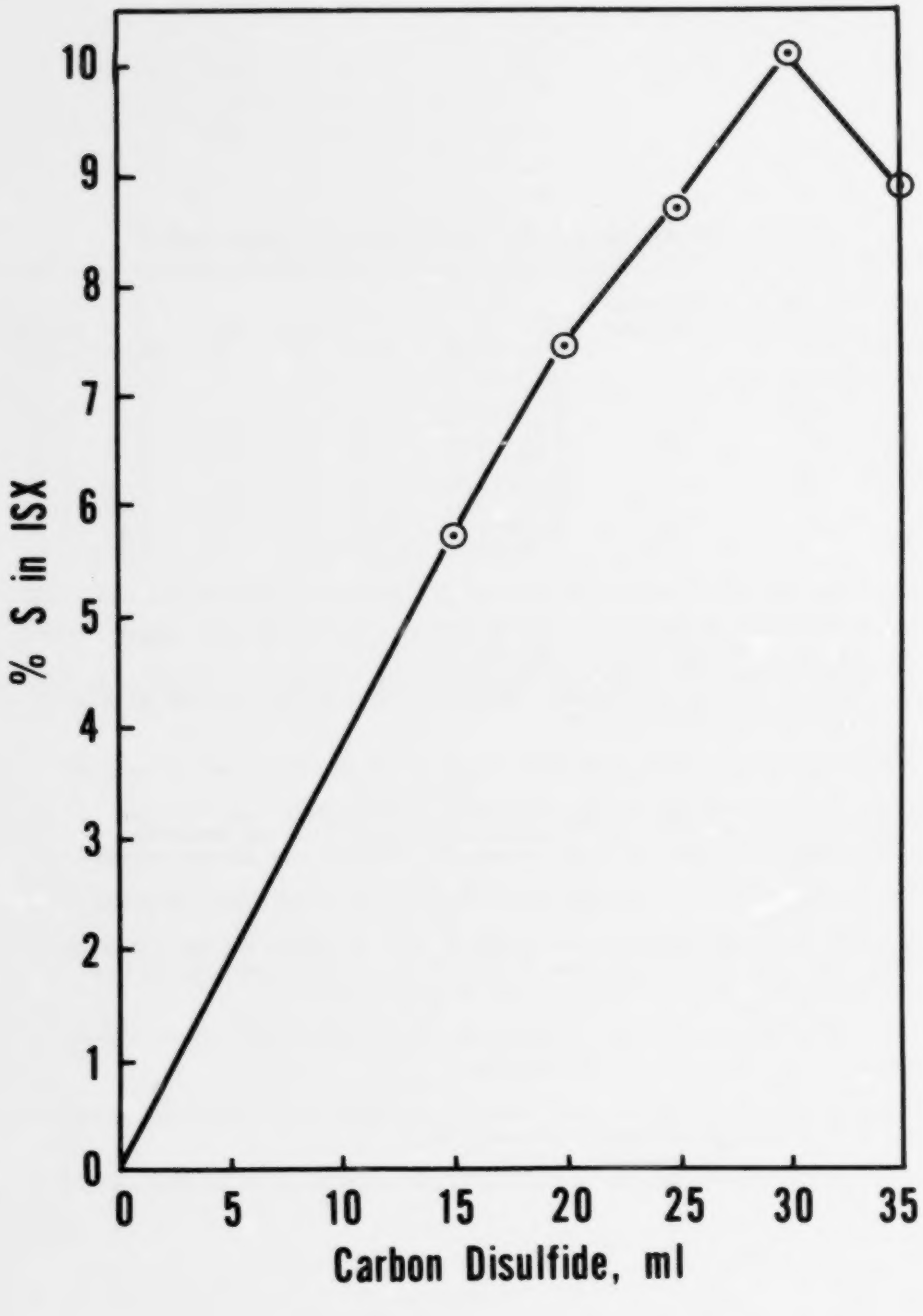


Figure 3. % S vs CS_2 charged in the xanthation of crosslinked starch.

TABLE 3. PREPARATION AND ANALYSIS OF INSOLUBLE STARCH XANTHATE

Cross-linked starch*	Carbon disulfide, ml	Magnesium† sulfate, g	% S d.b.	%H_2O‡	% Ash§	Na,# mg	Mg,# mg	Na/Mg	Capacity,** meq/g
A	15	12.4	5.76	2.19	10.72	8.5	6.2	1.37	0.88
A	20	15	7.44	1.34	16.52	10.6	6.9	1.54	1.14
A	25	17	8.70	1.40	19.20	12.1	7.0	1.73	1.20
A	30	19	10.12	0.85	24.08	14.2	7.4	1.92	1.56
A	35	21.5	8.86	1.74	18.15	13.2	8.3	1.59	1.36
A	30	18††	8.05‡‡	1.33	13.31	11.4	7.1	1.60	1.24
B	30	18††	9.29‡‡	0.86	16.32	12.8	7.3	1.75	1.44

* A. Epichlorohydrin crosslinked starch (HPD-53-91E, The Hubinger Company, Keokuk, Iowa). 9.09% H_2O; 100 g (0.56 mole, dry basis).
B. Vulca 90 (National Starch and Chemical Corp., Bridgewater, N.J.). 11.0% H_2O; 100 g (0.55 mole, dry basis). Additional water may be required to promote easy stirring with Vulca 90.

† Approximately 2 g magnesium sulfate for each 1% S in the product is optimum.

‡ These products were only flash dried using a Benco Bench Scale Vertical Pneumatic Dryer at 170°C and 305 m/min air velocity (1.5 sec residence time); therefore, lower moisture values were obtained over solvent drying.

§ % Ash includes sodium and magnesium of xanthate and bound alkali in product.

A 0.25-g sample was treated with 1N HNO_3 (45 ml) to remove all the sodium and magnesium. The filtrates diluted to 1 l and Na and Mg concentrations were determined on a Varian Techtron AA 120 spectrophotometer.

** $\% \text{ S} = \dfrac{6400 \text{ D.S.}}{162 - \text{D.S.} + 99.5 \text{ D.S.}}$, meq metal ion/g $= \dfrac{\text{D.S. } (1{,}000)}{162 + 99.5 \text{ D.S.}} = \dfrac{\% \text{ S}}{6.412}$
where D.S. is the degree of substitution.

†† Magnesium sulfate (18 g) in water (180 ml) was added 45 sec after the carbon disulfide and the reaction was allowed to proceed 1 hr.

‡‡ Lower sulfur values were due to the additional water used in the preparation.

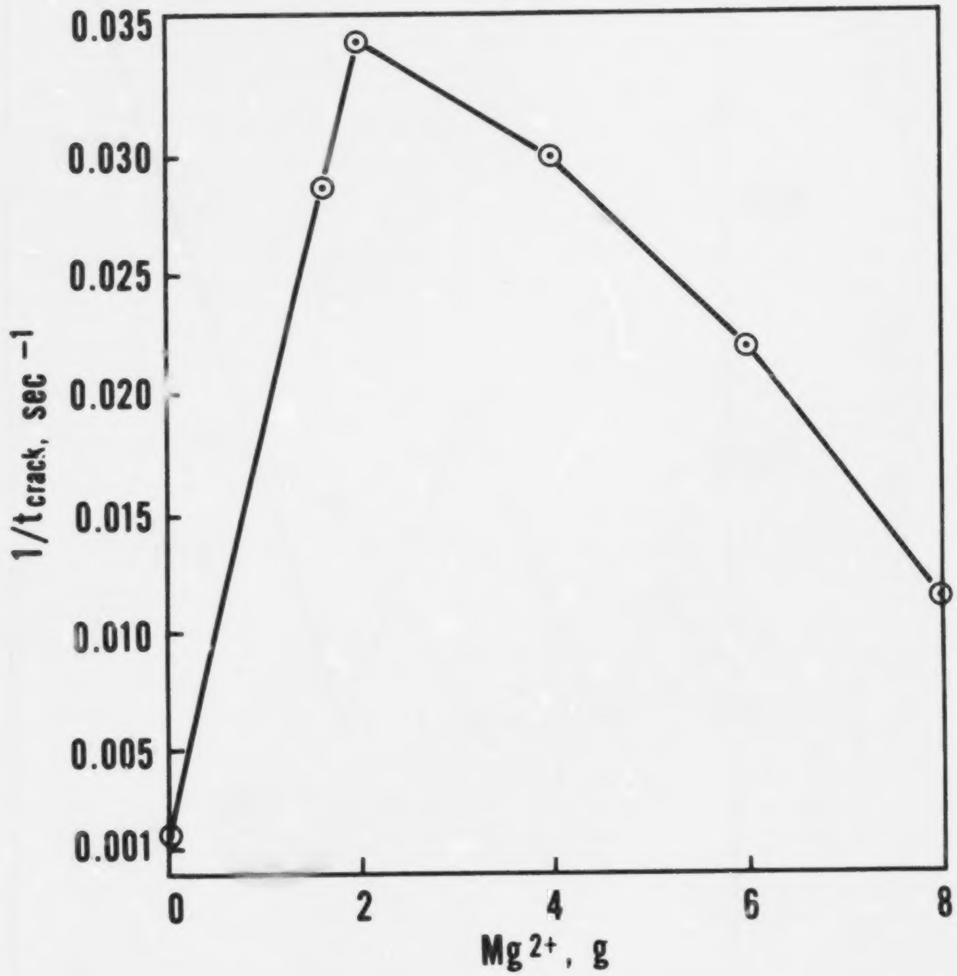


Figure 4. Amount of magnesium ion (Mg^{+2}) required for optimum ISX filtration rate.

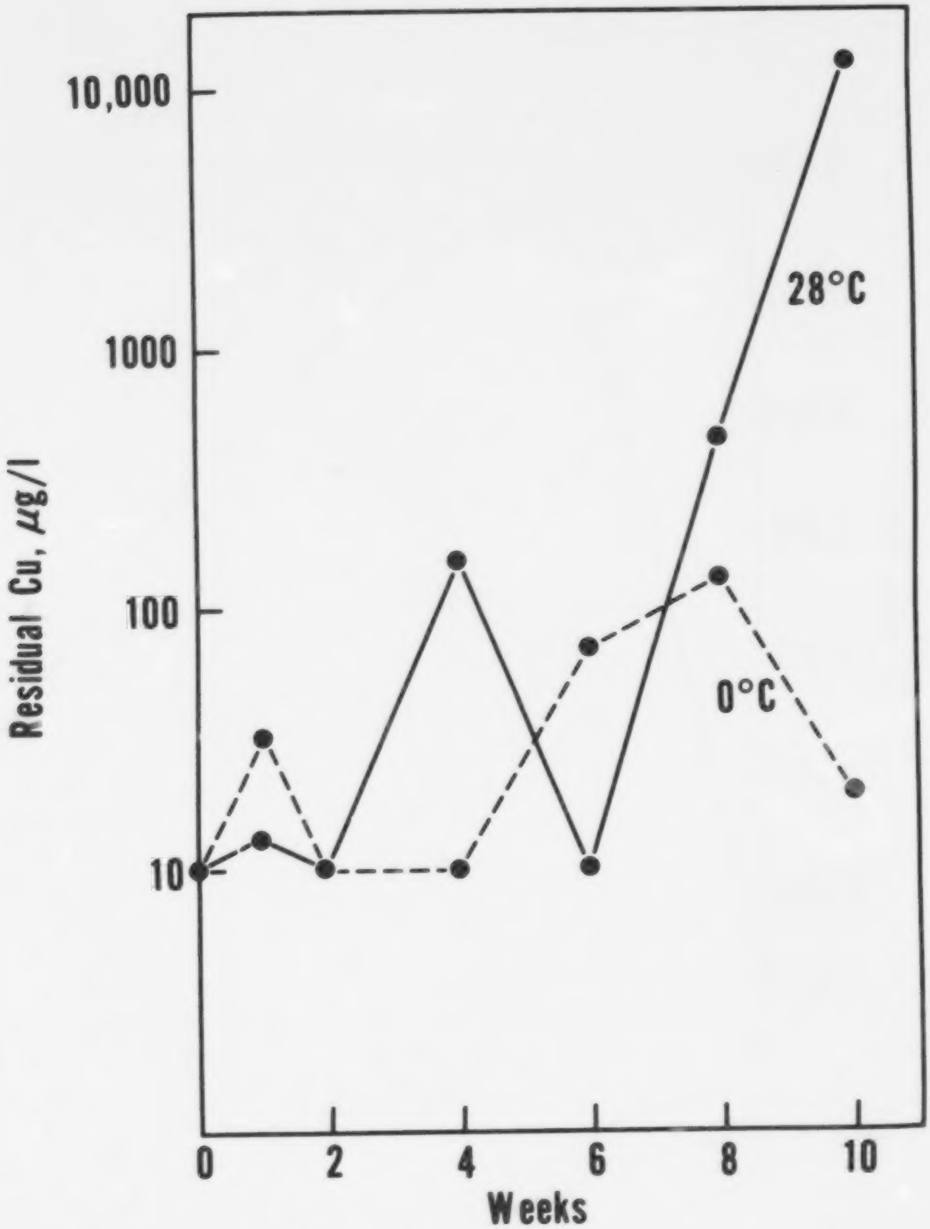


Figure 5. ISX stability-copper removal.

The moisture content of the stored ISX is very critical to product stability. Samples having moisture contents of <2% can be stored for several weeks at 28°C; however, samples having moisture contents >2% decompose faster. ISX of any moisture content, however, can be stored without decomposition at 0°C. Samples of ISX which have decomposed have a pink-orange color and a pungent odor.

Several additional things were tried to increase the stability of the ISX further. The products described in Tables 4 and 5 did show some increase in stability. The use of additional wash water only washes residual caustic from the product (Table 4) and the first two liters of wash water contained 98% of the caustic and salts from xanthation. In fact, 90% of the dissolved solids were removed after 1 l of wash. The removal of most of the excess caustic should aid drying of the ISX, and also in storage and stability because of the hygroscopic nature of sodium hydroxide.

Using additional amounts of magnesium sulfate in the wash water (Table 5) was evaluated since a completely substituted magnesium starch xanthate was a highly room temperature stable product (4). These washings wash out excess caustic and also substitute magnesium for some of the sodium on the xanthate forming magnesium starch xanthate. The magnesium starch xanthate portion is only effective in metal removal at pH's above 7 because it dissociates easier at that pH. This $MgSO_4$ wash treatment would, however, yield an effluent higher in dissolved solids.

Since the mother liquor of the xanthation of starch contained a considerable quantity of base and since large volumes of water would be required in the large-scale production of ISX, the reuse of the mother liquor was evaluated. Product analysis (Table 6) shows very little difference in the products. The increase in dissolved solids in the liquor had no effect on the subsequent xanthation. The eventual discharge of this caustic process water could be used to neutralize acidic process waters.

Evaluation of several drying procedures showed that ISX could be effectively dried by flash-, spray-, or freeze-drying. Sodium ISX, without the $MgSO_4$ treatment, could not be flash dried because it was slimy to feed. Drum drying of ISX is a possible means of drying. Oven- and rotary vacuum-drying led to considerable product decomposition in the few trials attempted.

Some additional observations about ISX are: (a) Some ISX samples appeared to decompose faster in direct light (>3% moisture content). (b) If dry ISX (1% moisture) is left in the open it will absorb water, and with time, will decompose to lose all its sulfur. (c) The smaller the Na/Mg ratio, the more stable the product; however, there appears to be some decrease in metal removal ability at pH's less than 7.0 if the ratio is smaller.

The ISX can be made in large quantities by several methods. One method would be to use a large, enclosed, stirred reactor in place of the covered beaker which was described previously, followed by centrifugation, washing, and drying. Another method which was evaluated successfully was to meter-in a caustic solution and carbon disulfide separately into a high shear continuous mixer, mixing these with a flowing stream of the crosslinked starch-

TABLE 4. ISX PREPARATIONS USING ADDITIONAL CAKE WASH WATER*

Wash-water volume, ml	Product wt, g	% S, d.b.		% H_2O		% Ash, d.b.		Na, mg	Mg, mg	Na/Mg	Capacity meq/g
		solvent	flash	solvent	flash	solvent	flash				
1000	147.2	10.90	11.86	9.88	0.80	22.72	14.80	10.00	5.83	1.71	1.85
1500	140.0	10.31	10.88	9.05	0.69	19.74	16.93	10.29	5.64	1.82	1.70
2000	137.2	9.70	11.00	3.48	0.86	17.98	18.12	10.00	7.17	1.39	1.72
3000	135.2	9.27	10.20	8.54	0.90	17.11	16.32	9.14	7.50	1.22	1.59
4000	134.6	9.08	10.18	9.17	0.82	15.02	16.57	10.29	8.33	1.23	1.59

* ISX was prepared using General Laboratory Preparation except wet cake was washed with additional water. See Table 3 for other notations.

TABLE 5. ISX PREPARATIONS USING ADDITIONAL MAGNESIUM SULFATE IN CAKE WASH WATER*

Weight $MgSO_4$ in wash water, g	Product wt, g	% S, d.b.		% H_2O		% Ash, d.b.		Na, mg	Mg, mg	Na/Mg	Capacity, meq/g
		solvent	flash	solvent	flash	solvent	flash				
0	140.0	10.31	10.88	9.05	0.69	19.74	16.93	10.29	5.64	1.82	1.70
10	139.7	8.32	9.47	8.17	0.19	16.42	14.15	6.71	9.72	0.69	1.47
20	142.1	8.09	9.52	9.62	2.18	14.94	14.64	6.43	10.89	0.59	1.48
30	149.1	7.51	8.87	13.49	2.02	6.08	5.20	1.20	13.89	0.09	1.38

* ISX was prepared using General Laboratory Procedure except wet cake was washed with indicated weight of $MgSO_4$ in water (500 ml) and then with water (1,000 ml). See Table 3 for other notations.

TABLE 6. REUSE OF MOTHER LIQUOR IN THE XANTHATION OF CROSSLINKED STARCH*

Wt NaOH added, g	Product wt, g	% S, d.b.		% H_2O		% Ash, d.b.		Na, mg	Mg, mg	Na/Mg	Capacity, meq/g
		solvent	flash	solvent	flash	solvent	flash				
45	140.0	10.31	10.88	9.05	0.69	19.74	16.93	10.29	5.64	1.82	1.70
38.85	144.5	11.33	12.07	8.76	0.72	23.29	20.53	11.14	6.61	1.68	1.88
39.35	144.5	10.93	11.42	8.45	0.49	18.58	17.51	11.00	6.86	1.60	1.78
39.57	141.8	9.38	10.07	11.52	0.49	16.73	15.35	9.80	7.25	1.35	1.57

* ISX was prepared using the General Laboratory Preparation by adding the indicated amounts of NaOH to 560 ml of the mother liquor of the preceding xanthation. See Table 3 for other notations.

magnesium sulfate slurry. This method shortens the xanthation time to about 30 min due to the excellent mixing; however, an additional hold time (30 min) would be required to obtain maximum xanthation. After the addition of some water to thin the thickened slurry, the product was centrifuged, washed, and dried (flash and freeze). Using the described experimental procedure, products were obtained which corresponded to beaker-prepared products.

A particle size distribution was run on a freeze-dried ISX sample using a Sharples Micromerograph. Figure 6 shows the particle size (95%) to fall between 5-40 microns. Even though ISX has a small particle size, the settling rate of the metal-ISX precipitate is very efficient. Scanning electron microscope photographs of ISX particles showed them to be of irregular shape and non-porous similar to starch granules.

As a measure of the binding ability of ISX for metal ions, Table 7 shows the solubility product constants for several metal ethyl xanthates (50). Values for the metal-ISX should correspond very closely with those listed. The higher the sulfur content of the ISX, the greater its capacity for heavy metal binding. The pH of the effluent to be treated should be pH 3 or higher since ISX is unstable at lower pH's. The ISX used in all the metal removal studies in this report still contained some sodium hydroxide, so when stoichiometric quantities were added to the unbuffered metal solutions a rise is pH to above 7 was observed. If the pH does not rise above pH 7, caustic should be added since maximum removal for most metals to below discharge limits (Tables 8-11) occurs above this pH.

The data in Tables 8 and 9 shows that ISX is effective in lowering metal concentrations to below stringent discharge limits from synthetic solutions. When ISX was compared (Table 10) with sodium hydroxide and calcium hydroxide, the ISX treatments resulted in lower residual metal concentrations. ISX has been shown effective in metal removal for many different industrial effluents (Table 11).

The ISX can be added as a solid or as a slurry to either batch type or continuous flow systems. Most heavy metal cations are removed instantaneously so only a short contact time is required; however, up to 60 min contact is not detrimental to removal (Table 12) and in most cases increases removal. In some cases less than stoichiometic quantities of ISX give excellent removal. This is probably caused by the pH increase with ISX. Salt concentrations of 0-10% in wastewaters have little influence on metal removal by ISX as shown by copper removal in the presence of sodium chloride (Table 13). Metals of any concentration can be removed with theoretical amounts of ISX (Table 14); however, concentrations over 100 mg/1 might not be economically favorable.

The effluent after an ISX treatment contains only sodium and magnesium ions from the ISX. The BOD and COD of treated effluents are not increased due to ISX treatment and in some cases are even lowered. Therefore, effluents treated with ISX offer a possibility of water reuse. There is no detectable sulfur byproduct in the treated effluent unless a decomposed ISX is used. The use of an ISX which has decomposed slightly will sometimes turn the effluent pink-amber, but at a pH above 8.5 these metal-bearing decomposition products usually precipitate leaving a clear colorless effluent.

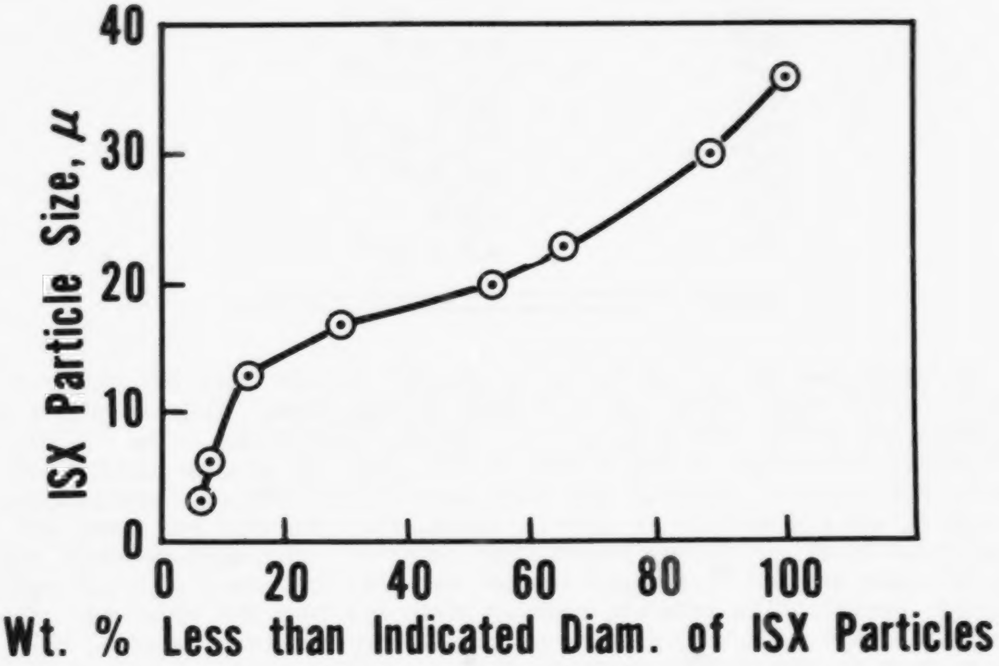


Figure 6. Particle size distribution of ISX.

TABLE 7. SOLUBILITY PRODUCT CONSTANTS FOR METAL ETHYL XANTHATES (50)

Metal	Ksp, metal ethyl xanthate
Ag^{1+}	5×10^{-19}
Au^{1+}	6×10^{-30}
Bi^{3+}	$\sim 10^{-31}$
Cd^{2+}	2.6×10^{-14}
Co^{2+}	5.4×10^{-13}
Cu^{1+}	5.2×10^{-20}
Fe^{2+}	8×10^{-8}
Hg^{2+}	1.7×10^{-38}
Mn^{2+}	$>10^{2+}$
Ni^{2+}	1.4×10^{-12}
Pb^{2+}	1.7×10^{-17}
Sb^{3+}	$\sim 10^{-24}$
Sn^{2+}	$\sim 10^{-8}$
Zn^{2+}	4.9×10^{-9}

An effective way to use ISX is to precoat filters with ISX and filter aids then pass metal containing effluents through them. This technique would eliminate any gravity settling or centrifuging separations. The ISX alone can be initially precoated on the filter or the metal-ISX sludge could be separated in this manner. Several runs were made using different combinations of ISX and filter aid media. If care is taken, the cake will not crack and in these cases excellent copper removal was observed (<0.1 mg/l residual copper). When the cake cracked the copper removal was less efficient (0.5-6.6 mg/l residual copper). The cake was removed after all runs and observed. The top layer was always a dark gold color of an ISX-copper sludge, whereas the section next to the filter paper was the pale yellow color of unused ISX. One run was made using the filter containing a 0.6 cm layer of filter aid only and then passing through it a copper-ISX slurry. The residual copper on this run was less than 0.02 mg/l from an initial copper concentration of 82.8 mg/l. In all the runs, the increase in pressure drop was negligible which would indicate the metal-ISX is more filterable than gelatinous hydroxide precipitates.

More specific information on the use of ISX as a precoat is being generated by an industrial company. Data supplied by company officials agrees with our findings. Another company has installed this technique in their plating shop for heavy metal removal from plating rinse solutions. Three pressure filters are precoated with ISX only every 2 weeks and the rinse waters from a copper plating line, a nickel plating line and a tin-lead line are passed through the three filters separately. Even though the rinses are passed

TABLE 8. REMOVAL OF HEAVY METAL CATIONS FROM WATER WITH ISX*

Metal	Initial conc., mg/1	ISX, g	Residual conc., mg/1	Illinois discharge limit, mg/1
Ag^+	53.94	0.32	0.016	0.005
Au^{3+}	30.00	0.50	<0.010	---
Cd^{2+}	56.20	0.64	0.012	0.050
Co^{2+}	29.48	0.64	0.090	---
Cr^{3+}	26.00	0.64	0.024	1.0
Cu^{2+}	31.77	0.32	0.008	0.020
Fe^{2+}	27.92	0.32	0.015	1.0
Hg^{2+}	100.00	0.64	0.001	0.0005
Mn^{2+}	27.47	0.64	0.015	1.0
Ni^{2+}	29.35	0.64	0.160	1.0
Pb^{2+}	103.60	0.64	0.035	0.100
Zn^{2+}	32.69	0.32	0.294	1.0

* Synthetic solutions (1,000 ml) containing the individual metals at the indicated concentration were treated with the indicated amount of ISX (capacity = 1.56 meq metal ion/g) at pH = 3.7. Solutions were stirred for 5-60 min at a final pH of 8.9. After filtration, the residual metals were determined by a Varian Techtron AA 120. The theoretical weight of ISX for a divalent metal is 0.64 g. Value listed with less than (<) was below detection limit.

through the cakes periodically, the average residual metal concentrations are copper (0.06 mg/1), nickel (0.57 mg/1), and tin-lead (0.33 mg/1-0.09 mg/1). This system has been in operation for 20 months with complete water recycle.

Complexed metals sometimes can be effectively removed with ISX; however, this depends totally on the complexing agent. Copper complexes with EDTA, NTA, citrate, tartrate, gluconate, and pyrophosphate are only partially removed with ISX. If the pH of solutions of these complexes are lowered to a pH 2.5-5.0, the complex dissociates and more effective copper removal is attainable. The copper-ammonia complex [$Cu(NH_3)_4^{2+}$) which is still positively charged is effectively removed by ISX (see Copper Etchants under Circuit Board Effluents). A consulting engineering firm has found that ISX effectively removes copper from a copper-dye complex and has designed a 4.75 million 1/day treatment facility using ISX as a copper scavenger. Another company has found ISX effective in removal of a copper-lignin complex (100 mg/1 copper) at 90°C and pH 13-14. The presence of lime had no effect on the effectiveness of ISX in this system.

The metal-ISX sludge settles fairly rapidly (95-98% settled in 10 min) and the sludge can be removed by a clarifier, centrifuge, or filter. The sludge obtained from a filter using small quantities of ISX is around 50%

TABLE 9. REMOVAL OF METALS FROM DILUTE SOLUTION WITH ISX*

Metal	Initial conc., mg/l	Residual conc., mg/l
Cd^{2+}	5.62	0.001
Co^{2+}	2.95	<0.010
Cr^{3+}	2.60	0.026
Cu^{2+}	3.18	<0.005
Fe^{2+}	2.79	0.001
Hg^{2+}	100.00	0.0007
Mn^{2+}	2.75	0.010
Ni^{2+}	2.93	<0.050
Pb^{2+}	10.36	<0.031
Zn^{2+}	3.27	0.007

* A synthetic solution (1,000 ml) containing a mixture of heavy metals of the indicated concentrations at pH 3.5 was treated with ISX (capacity = 1.56 meq metal ion/g, 0.32 g) to a final pH = 8.9. After filtration the residual metals were determined by a Varian Techtron AA 120. Values with less than (<) were below detection limits.

solids which allows its handling ease. After 3 hr drying under ambient conditions, the thin cakes increase to 90% solids. Thicker cakes would require several days for drying (Table 15).

The metal-ISX can be landfilled or treated for metal recovery. If the sludge is landfilled, the metal is bound fairly strongly and would have less chance to be leached out than with a hydroxide sludge.

Recovery of the metal from ISX-metal sludge is possible by acid stripping or incineration. The use of soluble complex eluting agents (EDTA, etc.) has been totally ineffective in metal removal from a metal-ISX sludge. Several acid stripping procedures were evaluated to recover a concentrated solution of the metal ions and to recover the crosslinked starch for rexanthation. When a copper-ISX sludge was treated with 6N HCl or 18N H_2SO_4, ineffective copper recovery was obtained (7% and 2.8%, respectively). However, when 4N HNO_3 was evaluated, complete copper recovery was obtained (see p. 13). The same has been found true for all metals evaluated except gold (0% stripped) and mercury (3% stripped). Contacting the ISX-metal sludge with sodium or magnesium salts showed no exchange with the copper.

TABLE 10. HEAVY METAL REMOVAL FROM 95 LITERS OF WATER*

Treatment	Chemical added	Amount† added	pH	Cd µg/l	Cr µg/l	Cu µg/l	Fe µg/l	Pb µg/l	Mn µg/l	Hg µg/l	Ni µg/l	Ag µg/l	Zn µg/l	COD mg/l
I	None		6.5	5440	2790	3260	3030	3670	2740	9900	2960	62	2020	
	ISX‡	103 g	7.0	13	18	9	111	0	2380	54	23	4	13	61
II	None		2.3	5260	2930	3350	3040	4130	2670	9960	2850	62	2900	
	NaOH§	190 ml	6.5	5260	1150	1520	47	1740	2630		2830	49	2820	
	NaOH	2 ml	7.0	5100	436	1450	486	2290	2630		2810	56	2590	128
	NaOH	10 ml	7.5	4740	143	630	139	1100	2630		2790	68	1700	
	NaOH	6.5 ml	8.0	3610	36	108	14	46	2420		2380	52	36	142
	NaOH	23.5 ml	9.0	1130	53	76	72	183	1579	<100	790	47	56	
III	None		6.7	4740	1040	1110	1110	2940	2780	9800	2920	36	2510	
	$Ca(OH)_2$#		6.5	4690	36	985	50	1650	2420		2560	36	2770	
	$Ca(OH)_2$		7.0	4460	18	477	11	275	2320		2460	16	2200	82
	$Ca(OH)_2$		7.5	3890	14	246	17	46	2260		2310	31	1370	
	$Ca(OH)_2$		8.0	3140	14	68	17	46	2100		2270	41	110	82
	$Ca(OH)_2$		9.0	330	14	10	17	23	990		1540	31	10	
	$Ca(OH)_2$	200 ml	10.0	9	14	10	17	23	0	<100	23	21	10	
IV	None		6.5	5050	7	65	28	826	2840	9900	3000	47	2310	
	NaOH	13 ml	7.0	4720	125	237	150	826	2840	9900	2710	36	1920	
	ISX	16 g	7.5	3530	0	88	14	183	2740	150	2100	16	1100	
	ISX	24 g	8.0	19	0	26	17	46	2630	92	115	2	51	34
	ISX	32 g	8.5	8	0	14	17	23	1900	1.5	23	2	10	
V	None		3.3	5930	2930	3230	2670	6330	2950	9850	2850	83	2920	
	NaOH	19 ml	6.5	5460	0	72	17	2940	2840		2770	62	2350	
	NaOH	1 ml	7.0	5500	0	14	17	692	2740		2520	47	2000	
	ISX	5.5 g	7.5	4840	0	4	0	0	2590	140	1770	26	740	
	ISX	6.0 g	8.0	2010	0	3	1	0	2020	93	15	42	5	21
	ISX	11 g	8.5	6	0	0	17	0	0	29	6	0	5	23
Concentration of metal added				5620	2600	3180	2790	10360	2750	10000	2940	5390	3270	
Illinois Discharge Limit				50	1000	20	1000	100	1000	0.5	1000	5	1000	

* Treatments I-IV were in 95 l of tap water. Treatment V was in distilled water.

† The chemicals were added in the increments shown to reach the pH listed.

‡ ISX (1.1 meq metal ion/g).

§ NaOH (200 g/l).

# $Ca(OH)_2$ (200 g/l).

TABLE 11. TREATMENT OF INDUSTRIAL EFFLUENTS WITH ISX*

Industrial effluent	Initial	ISX†	Final	Metal conc., μg/1						
sample	pH	wt, g	pH	Cd^{2+}	Cr^{3+}	Cu^{2+}	Fe^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}
Steel pickling rinse										
initial	7.5	---	---				34,640			
treated	---	0.0612	9.0				120			
Nickel plating rinse										
initial	7.6	---	---						923,000	
treated	---	0.9238	10.7						34	
Zinc mine drainage										
initial	3.5	---	---							4,836
treated	---	0.0315	7.7							16
Aerospace plating rinse										
initial	5.3	---	---	87	250,000	150	3,045	555		
treated	---	0.1596	6.7	5	216	16	0	0		
Aerospace plating rinse										
initial	5.3	---	---	150	19,444	105				
treated	---	0.0416	7.3	4	13	9				
Aerospace plating rinse										
initial	5.1	---	---	333	3,611	1,340	47,180	267	6,640	
treated	---	0.2892	6.2	13	744	16	3,227	0	55	
Aerospace plating rinse										
initial	4.4	---	---	147	2,833	105				
treated	---	0.0302	7.0	0	222	0				
Aerospace plating rinse										
initial	3.1	---	---	833		217				
treated	---	0.0510	7.5	17		0				
Chemical plating rinse										
initial	4.5	---	---	4,197	20,000	141,000		13,111		
treated	---	0.2452	7.1	15	17	100		166		

* Sample (50-ml) of industrial effluent treated as received.
† ISX (1.1 meq metal ion/g).

TABLE 12. EFFECT OF STIRRING TIME ON COPPER REMOVAL WITH ISX*

Stirring time, min	Residual copper conc., mg/1
1	0.02
5	<0.01
30	<0.01
60	0.02
120	0.06
240	0.08
480	0.08

* A solution (1000 ml) containing copper (31.77 mg/1) at pH = 4.0 was treated with ISX (0.653 g, 1.53 meq metal ion/g to pH = 8.9. Aliquots (10 ml) were removed at the indicated times and were filtered. The residual copper concentration was determined by a Varian Techtron AA 120 spectrophotometer.

TABLE 13. EFFECT OF COPPER REMOVAL WITH ISX IN THE PRESENCE OF SODIUM CHLORIDE*

NaCl, g	Residual copper conc., mg/1	Sludge color	% Copper removal
0	0.025	gold-brown	99.92
1	0.049	light gold	99.85
2	0.069	light gold	99.78
5	0.166	light gold	99.48
10	0.219	dark yellow	99.31

* Solutions (100 ml) containing copper (31.77 mg/1) and the indicated weight of NaCl were treated with ISX (0.063 g, 1.53 meq metal ion/g) at pH 3.7. Solutions were stirred 5 min to a final pH of 8.6. After filtration, the residual copper concentration was determined by a Varian Techtron AA 120.

TABLE 14. EFFECT OF COPPER CONCENTRATION ON COPPER REMOVAL WITH ISX*

Initial copper conc., mg/l	ISX, g	Final pH	Residual copper conc., mg/l
0.5	0.010	8.0	<0.01
1.0	0.020	8.1	0.05
5.0	0.103	8.7	<0.01
10.0	0.205	8.8	<0.01
50.0	1.025	9.2	0.04
100.0	2.050	9.2	0.03

* Solutions (1,000 ml) containing the indicated amounts of copper and ISX (1.53 meq metal ion/g) were stirred 5 min and filtered. The residual copper concentration was determined by a Varian Techtron AA 120 spectrophotometer.

TABLE 15. COPPER-ISX SLUDGE DEWATERING*

Days	Weight of sludge, g	% Solids
0	779	25.7
1	668	30.0
2	553	36.2
3	418	47.8
6	220	90.0

* A copper solution (100 mg/l, 25 gal) was treated at pH 4.0 with ISX (200 g, 1.5 meq metal ion/g) to a final pH of 8.8. After 5 min the slurry was filtered through a Büchner funnel until no visible water remained. The 3 cm sludge cake was crumbled and allowed to air dry at 22°C and 50% relative humidity. Theoretical sludge weight is 200 g.

TABLE 16. GOLD REMOVAL WITH ISX*

Final pH	Residual gold, mg/l
4	0.182
5	0.221
6	0.125
7	0.091
8	0.456
9.8	3.812

* Solutions (100 ml) containing gold (30.0 mg/l) were treated at the indicated pH's with ISX (0.05 g, 1.53 meq metal ion/g). After filtration, the residual gold was determined by AA.

A study was made to determine the most effective pH for gold removal with ISX. Table 16 shows that gold removal is best around pH 7 whereas for most other metals higher pH's give better removal with ISX. As previously mentioned, 4N HNO_3 was ineffective in recovering gold from an ISX sludge. Aqua regia (1 part HNO_3:3 parts HCl) was 100% effective in gold recovery and this would allow its recovery in a pure state (see p. 13).

The crosslinked starch recovered after 4N HNO_3 treatment of a metal-ISX sludge can be rexanthated for reuse. The acid treatment does destroy some of the crosslinking but at least one regeneration still yields an effective metal removal product. If a copper-ISX sludge is treated with 4N HNO_3, a product is obtained that still contains 50% of its sulfur (Table 17) and this starch xanthide is still very effective in metal removal above pH 7.

BRASS MILL WASTEWATER

Our major objective in treating the brass mill wastewater we chose was to lower the present total copper concentration from 0.2 mg/l to 0.02 mg/l so the wastewater could be discharged to an Illinois creek having a 0.02 mg/l copper discharge limit. Preliminary bench scale experiments using ISX in combination with filtration suggest that this objective may be achieved by a supplemental process to conventional treatments. Since the brass mill has a high volume flow (11.3×10^6 l/day), we tried to adopt methods that would be economically feasible for this industry.

TABLE 17. NITRIC ACID (4N) TREATMENT OF ISX PRODUCTS*

Material	Weight recovered, g	Product analysis % S	% H_2O	% Ash	% N
Crosslinked starch	88	0.05	6.84	0.44	0.10
ISX	65	0.07	6.88	0.41	0.06
Copper-ISX	78	8.14	5.08	0.53	0.11
Zinc-ISX	71	0.27	7.60	0.43	0.05

* The materials (100 g) were slurried in 4N HNO_3 (500 ml) for 30 min. After filtration and a water wash, the cake was reslurried and adjusted to pH 6.5 with 1N NaOH. The slurry was filtered, water washed, acetone dried, and air dried.

The results in this section were interpreted by making the following assumptions: (a) The copper content is the total copper present in whatever form it exists, i.e., as the unsettled copper-ISX complex, as Cu^{2+} or Cu^{1+} ion, or as the hydroxide, carbonate, or oxide. The predominant species will be governed primarily by the pH of the wastewater at the time of sampling. (b) The jar tests are on a comparative basis only, comparing the amount of total copper in suspension or solution at a fixed depth (3.2 cm), between samples having different additives, pH's, etc. (c) The brass mill wastewater samples evaluated were obtained at different times and some minor variations in our data are representative of slightly different composition of wastewater samples.

Preliminary jar test experiments were run on synthetic copper solutions to obtain information and techniques which could be applied to an actual brass mill wastewater. Since the brass mill wastewaters that we were working with contained approximately 200 µg/l copper at a pH of 9.0 to 9.5 after conventional treatment, our studies with synthetic copper solutions were conducted under these conditions. It is well known that at these pH's most of the copper will precipitate as the hydroxide and will be present as small colloidal particles. Sand filtration showed only limited removal (0-10%) starting with 200 µg/l total copper at pH 9.0, while millipore filtration (0.45 µ) showed consistent copper removal (80%) on settled supernatants. Figure 7 shows data which also corraborates the presence of colloidal copper hydroxide, since ISX is ineffective in removing colloidal copper hydroxide. The increase in copper concentration at the 25-mg ISX addition is probably due to additional copper-ISX fines in suspension. All figures in this section include settling curves at 10 and 30 min to show that longer settling times increase removal.

If the copper is present as colloidal copper hydroxide particles, coagulant aids such as alum should aid in its settling. Several evaluations using alum alone with synthetic copper solutions resulted in considerable copper

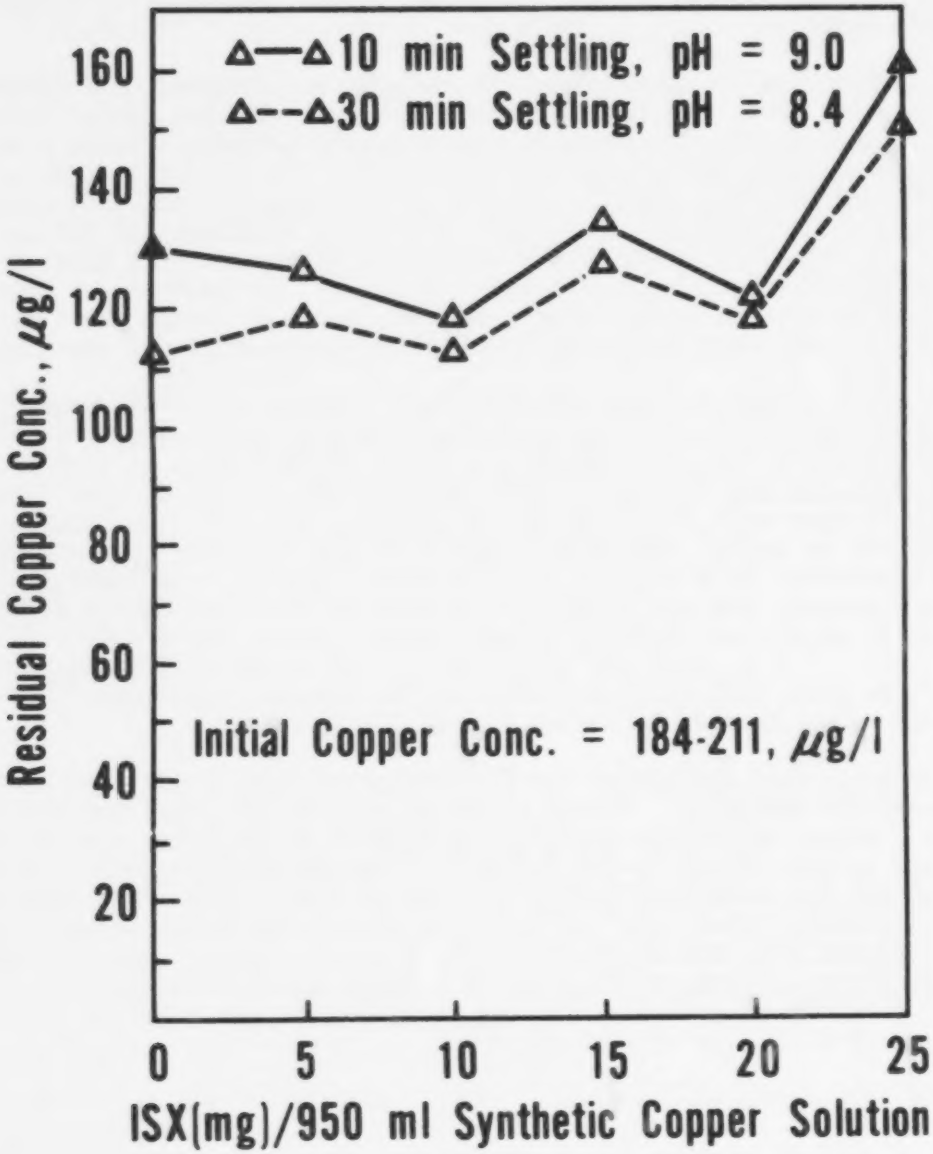


Figure 7. Treatment of synthetic copper solution with ISX only.

removal (20-80%) by settling of the colloidal copper hydroxide. Since alum additions always lowered the pH, the pH was always readjusted to 9 unless otherwise noted.

A combination treatment using ISX and alum at different concentrations (Figures 8-10) shows that both soluble copper and colloidal copper hydroxide can be lowered to very low residual copper concentrations. Figure 8 shows an evaluation at constant Al^{3+} (10 mg) and variable ISX (0-25 mg) at pH 9.0. Figures 9 and 10 report data to show the effectiveness of variable amounts of both ISX (5-15 mg) and Al^{3+} (0-25 mg). For these solutions ISX (15 mg) and Al^{3+} (10 mg) resulted in 95% copper removal in 10 min settling which is sufficient to reach strict discharge limits (20 μg/l). The addition of increasing amounts of alum gives greater copper removal, and even though there was some turbidity at the 10-min sampling, excellent copper removal was obtained.

Several synthetic copper solutions were screened with ISX, coagulant aids, and other additives using centrifugation as a means of separation. Several industries use centrifuges as a means of separation of sludges so copper solutions were evaluated over a broader concentration range. The data in Table 18 show results that were very erratic, from which no definite conclusions can be drawn. Since the majority of the suspended solids formed was copper hydroxide, it is assumed that the centrifugation techniques used in these experiments were not optimum. The data do show that the pH is very critical to obtain low residual copper concentrations. At the pH's we were working at (7.3-9.3), alum was more effective in coagulating the colloidal copper hydroxide, aiding its removal than the polymers evaluated. ISX showed some improvement in soluble copper removal (Table 18).

The brass mill wastewater was also evaluated using centrifugation and ISX, alum and other additives. Tables 19 and 20 show results that were more consistent. Longer spin times using ISX in batch centrifugation studies gave excellent results (Table 19 and Figure 11); however, this technique would not be practical for industries having large water flows. The use of alum also aided coagulation which resulted in more effective suspended particle removal. Table 20 shows data from continuous centrifugation studies. Even though the residual copper concentrations were still above desired concentrations, some general trends were observed. The use of ISX, alum, and polymers, if properly used, should aid in the removal of copper.

Preliminary jar test screening of ISX, coagulants, and other additives on the brass mill wastewater was performed and the results are shown in Tables 21-25. If the pH is above 8.5, alum or ferric ion alone will reduce the residual copper to 20 μg/l and/or remove greater than 90% of the total copper. However, if the pH was below 8.0, ISX or sulfide ion was needed along with the coagulant aid. Soluble starch xanthate alone compared to a commercial polyelectrolyte (Olin 5002) was less effective considering the dosage required. However, the addition of ISX to the soluble starch xanthate showed increased copper removal. A commercial polymer (Dearborn 420) showed improvement in copper removal with ISX and alum. In other studies, soluble starch xanthate (4.2 mg/l) in the pH range of 9.8-11.7 was equally effective in copper removal to commercial polymers (1.4 mg/l).

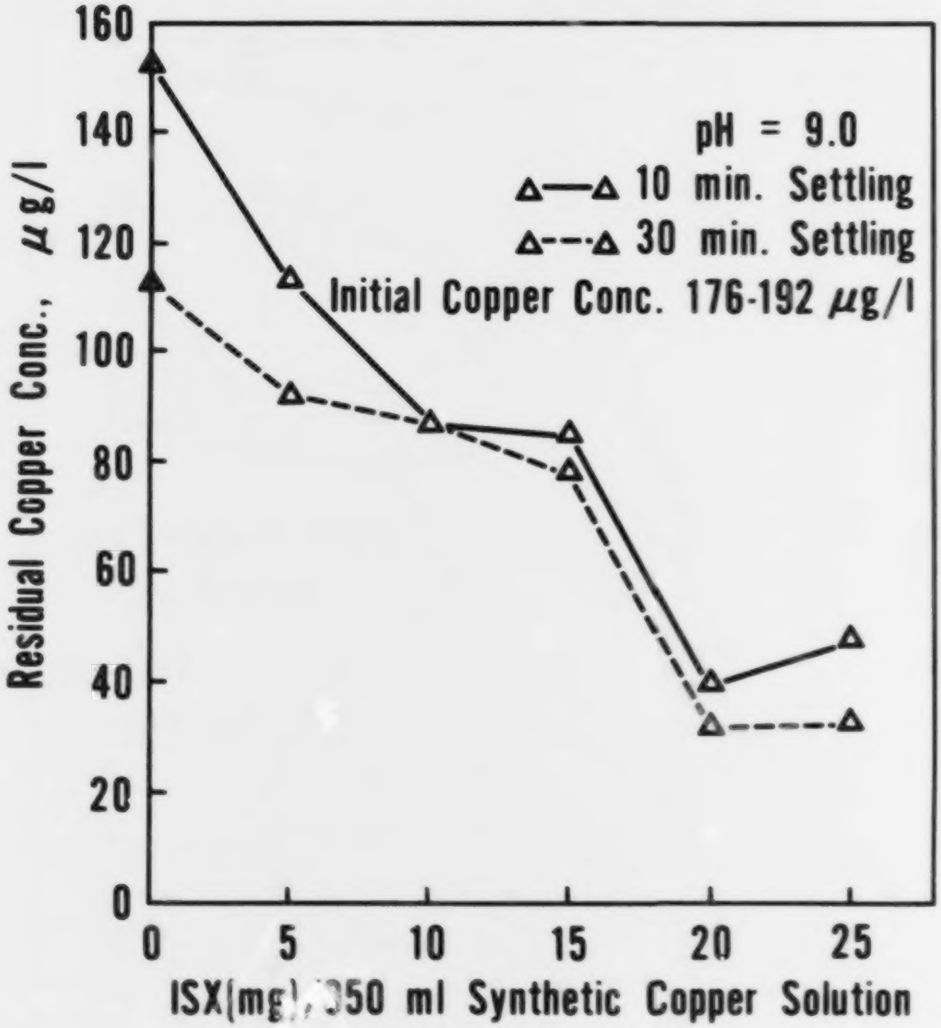


Figure 8. Treatment of synthetic copper solutions with ISX and Al^{3+}.

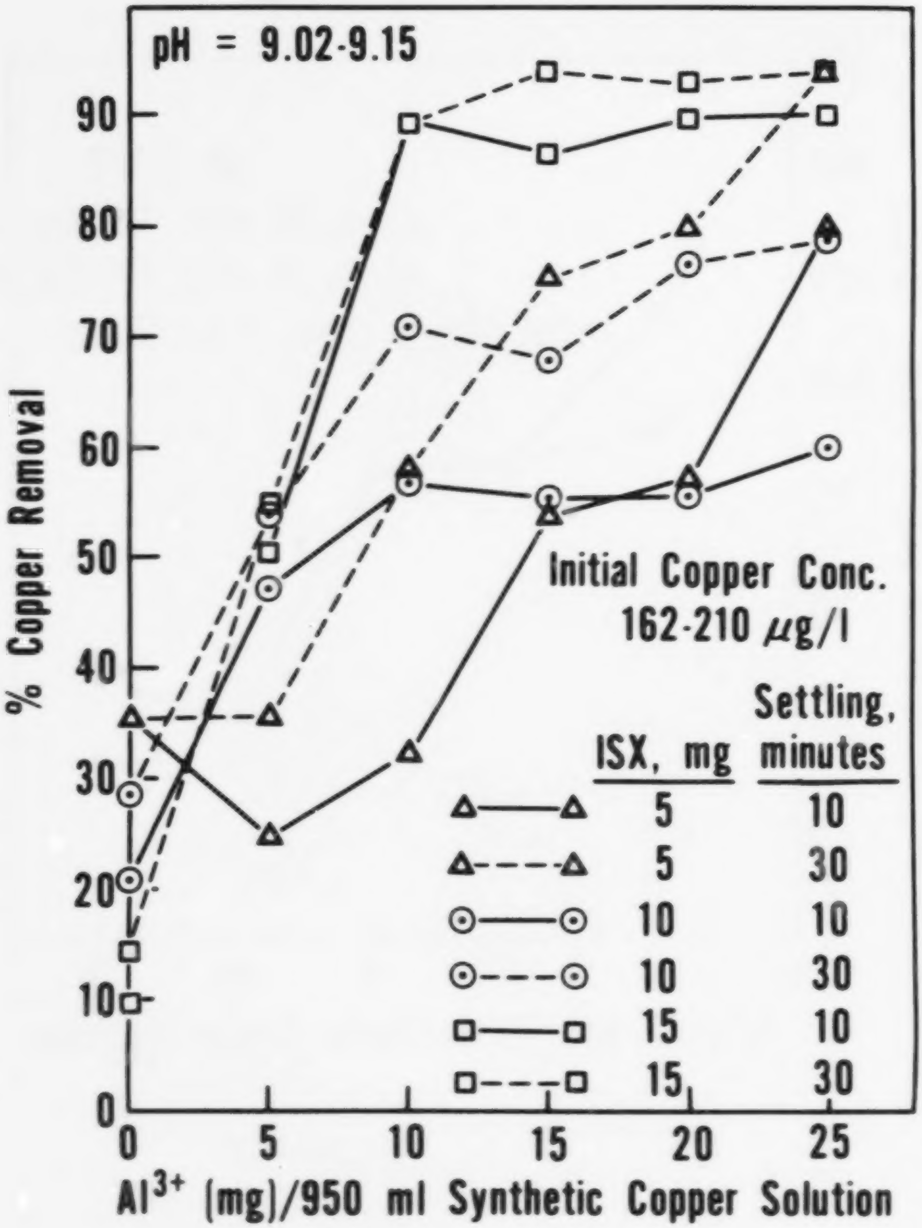


Figure 9. Treatment of synthetic copper solutions with Al^{3+} and ISX (% copper removal).

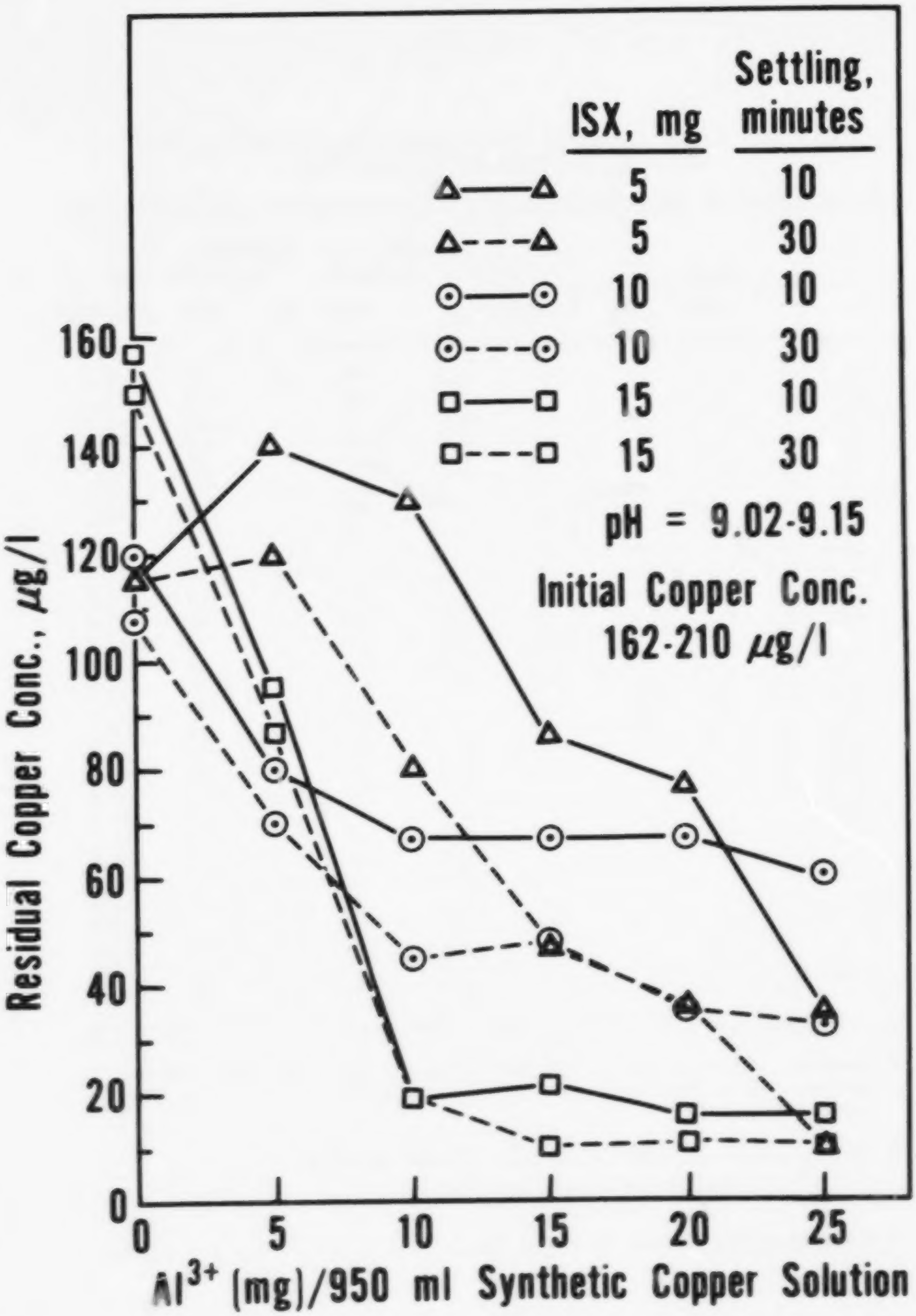


Figure 10. Treatment of synthetic copper solutions with Al^{3+} and ISX.

TABLE 18. COPPER REMOVAL BY CENTRIFUGATION FROM SYNTHETIC COPPER SOLUTIONS COMPARING SEVERAL ADDITIVES*

					Feed		Centrate		
mg/1						Total Cu		Total Cu	%
ISX	Al^{3+}	Na_2S	SSX†	polymer	pH	mg/1	pH	mg/1	Removal‡
26.4	---	---	---	---	9.6	306	9.6	140	54.2
627§	---	---	---	---	8.1	455	---	370	18.7
1,056§	---	---	---	---	8.0	20,700	---	3,620	82.5
20	---	---	---	---	8.0	3,860	---	870	77.5
20	---	---	---	4#	8.0	3,860	---	260	93.2
12	---	---	---	---	7.8	405	7.9	265	34.6
12	---	---	---	4#	---	405	---	240	40.7
10	---	---	---	---	---	159	8.4	150	5.7
10	---	---	4	---	---	159	8.4	140	11.9
---	---	---	---	---	8.5	189	8.8	160	15.3
21	---	---	---	---	9.0	235	---	100	57.4
20	---	---	---	4#	9.0	205	---	66	67.8
20	10	---	---	4#	9.0	205	---	40	80.5
2.6	---	---	---	4#	9.1	300	---	60	80.0
2.6	---	---	---	4#	9.1	300	---	160	46.6
5.7	---	---	---	---	---	244	7.3	244	0
5.7	---	---	---	4#	---	244	7.8	244	0
11.4	---	---	---	---	8.6	249	---	115	53.8
11.4	---	---	---	1.5#	8.6	202	---	110	45.5
11.4	10	---	---	3.0#	9.3	193	---	10	94.8
9.8	---	0.5	---	---	9.0	200	---	110	45.0
---	---	0.5	---	---	9.0	263	---	115	56.2
---	---	---	---	---	9.0	146	---	78	46.6
---	---	---	---	3.0#	9.0	146	---	70	52.1
---	---	---	---	---	9.3	245	---	10	95.9
---	10	---	---	---	9.3	243	---	0	100.0
---	---	---	---	---	9.35	341	---	193	43.4
---	---	---	---	4.0**	9.0	280	---	180	35.7
10	15	---	---	---	8.45	140	---	85	39.3

* Synthetic copper solutions (95-150 1) were treated with additives as indicated at a feed rate of 6.0 ± 0.3 LPM and 26,600 X G in the Super Centrifuge.

† Soluble starch xanthate (D.S. 0.11, freshly diluted).

‡ $\% \text{ Removal} = \frac{\text{Feed copper - centrate copper}}{\text{feed copper}} \times 100.$

§ Added in larger amounts to raise the pH.

Dearborn 420.

** Nalcoyte 676.

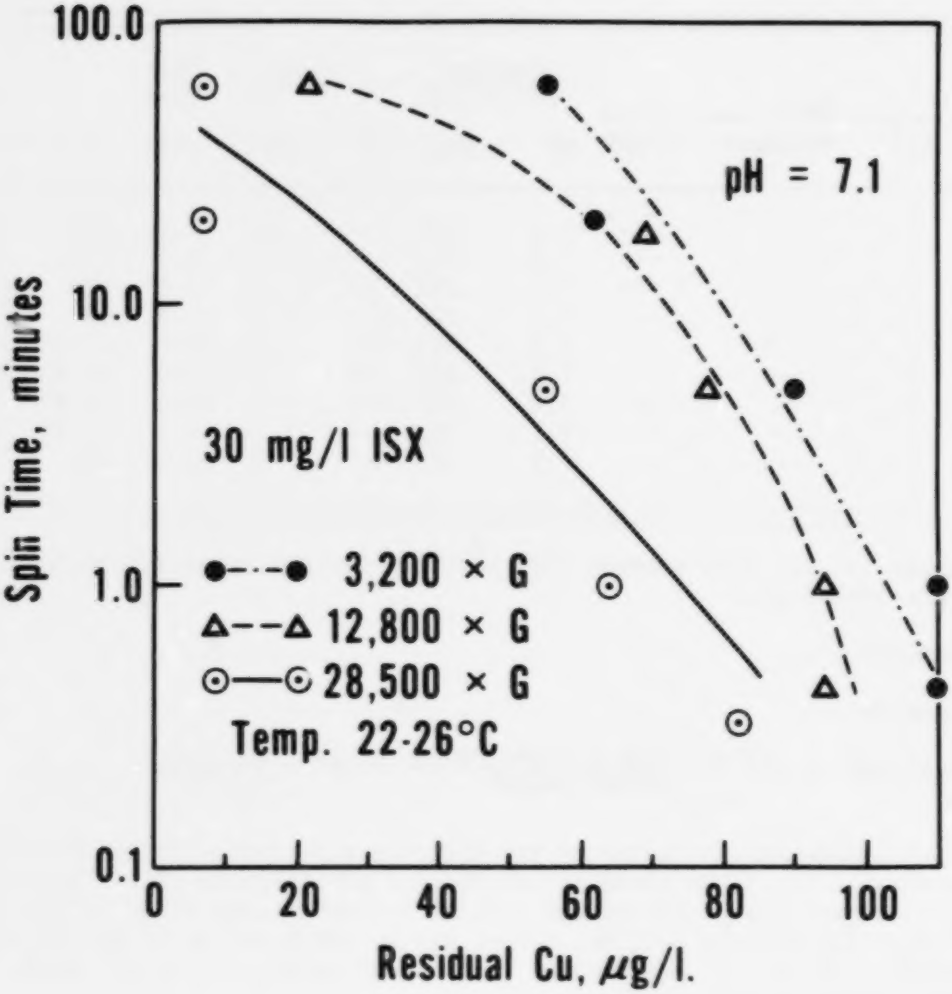


Figure 11. Laboratory batch centrifuging of brass mill wastewater with ISX only.

TABLE 19. COPPER REMOVAL FROM BRASS MILL WASTEWATER USING BATCH CENTRIFUGATION*

mg/l				Initial		Final		Spin time,		%
ISX	Al^{3+}	Polymer†	Clay‡	pH	Cu µg/l	pH	Cu µg/l	min	X G	Removal§
30	---	---	---	7.1	202	---	112	0.66	28M	44.5
30	---	---	---	7.1	202	---	104	1.0	28M	48.5
30	---	---	---	7.1	202	7.1	33	20.0	28M	83.6
30	---	---	---	7.1	202	---	15	60.0	28M	92.6
30	---	1.0	---	7.1	202	---	46	60.0	12.8M	77.2
30	5	---	---	7.1	202	---	29	60.0	12.8M	85.6
30	5	--	20	7.1	202	---	31	60.0	12.8M	77.7
30	5	---	---	7.1	202	---	22	60.0	12.8M	89.1
30	---	---	---	7.1	202	---	49	60.0	28M	75.7

* Samples (20 ml) were treated with additives as indicated and centrifuged in the Beta-fuge.

† Nalcolyte 676.

‡ Bentonite.

§ Calculated as $\frac{\text{Initial copper-final copper}}{\text{initial copper}}$ X 100 = % removal.

A comprehensive series of jar tests were performed on the brass mill effluent with ISX alone (0-25 mg) at various pH's (Figure 12). The reduction in total copper was 26-55% of the initial concentrations after 10 min of settling. The minimum residual copper values exhibited at 10 mg ISX were noted previously (Figure 7), however the theoretical amount of ISX to remove 200 µg soluble copper is only 3.3 mg.

The use of alum as a coagulant aid to promote faster settling of copper bearing solids was evaluated more completely on the brass mill wastewater. This additive was chosen because it is commonly used in water clarification. The addition of alum to brass mill wastewater samples resulted in a lowering of pH (Figure 13). If the pH is not adjusted to above pH 8.0, very little copper removal was observed and the solutions were all turbid. When samples were readjusted to 9.1 and 10.0 after using various alum dosages, good copper removal was obtained (Figure 14). Up to approximately 4 mg Al^{3+} the copper removal was poor; however, above 5 mg Al^{3+} copper removal increases to 90% at pH 10.0. All supernatants were clear in 1-2 min; however, the settled solids were voluminous and easily resuspended. Figure 15 shows that ferric ion as

TABLE 20. COPPER REMOVAL FROM BRASS MILL WASTEWATER USING A CONTINUOUS CENTRIFUGE*

mg/l					Feed§ Total Cu		Centrate Total Cu		%
ISX	Al^{3+}	Na$_2$S	SSX†	Polymer‡	pH	µg/l	pH	µg/l	Removal
3.1	---	---	---	---	8.1	224	8.1	100	55.4
3.1	---	---	---	4.0	8.1	224	8.1	85	62.1
11.4	---	---	---	---	8.6	224	8.8	108	55.3
11.4	---	---	---	2.0	8.8	242	8.9	86	64.4
5.7	---	---	---	3.0	8.6	200	---	110	45.0
---	---	---	---	---	7.6	219	7.5	170	22.4
---	10	---	---	---	7.1	346	7.2	160	53.7
5.0	10	---	---	---	6.95	243#	7.2	150**	38.3

* Samples (95 1) were treated with additives as indicated and centrifuged in a P-600 centrifuge and super centrifuge.

† Soluble starch xanthate.

‡ Dearborn 420.

§ Feed rate 6.0 ± 0.3 LPM; 26,600 X G (Super Centrifuge).

# Feed rate 4.0-10.0 LPM; 5,300 X G (P-600).

** Average of 6 centrate samples.

ferric chloride was also an effective coagulant and even slightly better than alum. The supernatants were all clear after 1-2 min of settling. Lime was used to adjust the pH to 9.0.

A series of studies was made to determine whether ISX with a coagulant aid would help to reduce the soluble copper concentration to below 20 µg/l. Figure 16 shows some typical results using varying amounts of alum and ISX on the brass mill wastewater. As little as 5 mg ISX and 5 mg Al^{3+} lowered the residual copper to below 10 µg/l. The samples having 10-20 mg Al^{3+} were slightly turbid with the turbidity increasing with alum content. The 10-min settling samples were analyzed for residual aluminum concentration (3.0, 3.8, 7.7, 10.0 mg/l). Numerous other evaluations were run on the brass mill effluents which were received over a 6-month period. The results obtained were very similar to the data of Figure 16. Figure 17 depicts data using ISX (10 mg) and Al^{3+} (0-10 mg) without pH adjustment back to 9.0. As the pH decreases with increasing Al^{3+} amounts the residual copper concentration increases but at 5 mg Al^{3+} it is still below the desired 20 µg/l.

TABLE 21. PRELIMINARY JAR TESTS ON BRASS MILL WASTEWATER COMPARING VARIOUS ADDITIVES*

mg/950 ml Wastewater								
ISX	Soluble starch xanthate†	Polyelectrolyte‡	Al^{3+}	Initial Cu µg/1	Final Cu µg/1	Final pH	% Reduction	Supernatant at sampling
0	0	0	0	211	200	8.8	5.2	Slightly turbid
0	4	0	0	211	200	8.8	5.2	Slightly turbid
0	12	0	0	211	183	8.9	13.2	Slightly turbid
5	4	0	0	211	177	8.8	16.1	Slightly turbid
10	8	0	0	211	171	8.8	18.9	Slightly turbid
15	12	0	0	211	166	8.95	21.3	Slightly turbid
0	0	0	0	211	185	9.05	12.3	Very sl. turbid
0	0	0.35	0	211	191	9.05	9.5	Very sl. turbid
0	0	0.7	0	211	179	9.05	15.1	Very sl. turbid
0	0	1.0	0	211	185	9.05	12.2	Very sl. turbid
0	0	1.4	0	211	185	9.05	12.3	Very sl. turbid
0	0	2.1	0	211	185	9.05	12.3	Very sl. turbid
0	0	0	0	217	168	8.6	22.6	Clear
0	0	0	0	217	158	8.6	27.2	Clear
5	0	0	5.2	217	25	6.7	88.5	Slightly turbid
5	0	0	0	217	147	8.7	32.2	Clear
10	0	0	5.2	217	20	6.8	90.8	Slightly turbid
10	0	0	10.4	217	20	6.1	90.8	Slightly turbid

---

* Samples (950 ml) were treated with the indicated additives and evaluated using standard jar test techniques. Samples were removed 3.2 cm below the surface after 10 min of settling.

† Soluble starch xanthate (D.S. 0.11, freshly diluted).

‡ Olin 5002.

TABLE 22. PRELIMINARY JAR TESTS ON BRASS MILL WASTEWATER COMPARING VARIOUS ADDITIVES*

mg/1					Initial Cu	Final Cu	Final	%	Supernatant
ISX	Al^{3+}	Na_2S	Fe^{2+}	Fe^{3+}	μg/1	μg/1	pH	Reduction	at sampling
0	0	0	0	0	224	174	8.3	22.3	Clear
0	0	0	0	0	224	182	9.2	18.7	Clear
0	5.2	0	0	0	224	56	6.6	75.0	Clear
0	10.4	0	0	0	224	61	6.0	72.5	Clear
0	0	15	0	0	224	167	8.8	25.4	Clear
0	10.4	15	0	0	224	5	6.2	99.0	Slightly turbid
0	0	0	0	0	211	159	8.4	24.6	---
10	0	0	15	0	240	114	8.5	52.5	---
10	0	0	0	0	200	108	8.4	46.0	Deep yellow color
10	7.8	0	20	0	211	20	7.8	90.5	---
0	0	0	0	0	257	50	8.2	80.5	Deep yellow color
0	10.4	0	0	0	231	105	8.2	54.5	---
0	0	0	0	0	213	135	9.1	36.6	Clear
10	0	0	0	0	197	97	9.1	50.7	Clear
10	0	0	0	15	165	13	8.8	92.4	Clear
10	7.8	0	0	0	206	10	8.9	95.1	Clear
0	0	0	0	20	197	15	8.8	92.4	Clear
0	10.4	0	0	0	219	7	8.5	96.8	Clear

* Samples (950 ml) were treated with the indicated additives and evaluated using standard jar test techniques. Samples were removed 3.2 cm below the surface after 10 min of settling.

TABLE 23. PRELIMINARY JAR TESTS ON BRASS MILL WASTEWATER COMPARING VARIOUS ADDITIVES*

mg/l			Initial Cu μg/l	Final Cu μg/l	Final pH	% Reduction
ISX	Al^{3+}	Polyelectrolyte†				
0	0	0	210	59	8.7	71.9
10	0	0	210	38	8.75	81.0
20	0	0	210	30	8.7	85.7
10	5.2	0	210	16	8.6	92.4
20	10.4	0	210	3	8.6	98.7
0	10.4	0	210	19	8.6	90.9
0	0	0	83	40	9.05	51.8
10	2.6	4	83	2	8.8	97.6
10	5.2	4	83	7	8.8	91.4
10	7.8	4	83	2	7.9	97.6
10	10.4	4	83	2	6.8	97.6
10	5.2	12	83	2	7.2	97.6

* Samples (950 ml) were treated with the indicated additives and evaluated using standard jar test techniques. Samples were removed 3.2 cm below the surface after 10 min of settling.

† Dearborn 420.

Some of the information presented shows that the use of coagulants (alum or ferric chloride) alone will lower copper concentrations to below the desired 20 μg/l. Even though this was found to be true occassionally, the only consistent copper removal to below 20 μg/l was obtained with Al^{3+} (>10 mg) and ISX (>10 mg). To be certain of these evaluations on-site testing was performed on fresh brass mill wastewaters. Figure 18 shows the results of this testing. From the curves it is apparent that pH adjustment is required and that ISX is required to reach 20 μg/l residual copper.

Company representatives have worked closely with us on our evaluations and the data generated from this study will be very useful to this type of industry in reducing high residual copper concentrations in their effluent, however considerably more work must be done to generage data using ISX in a technically feasible and economically reasonable treatment process for wastewaters containing heavy metals in a large volume, continuous flow facility. Further scale-up of these techniques to a pilot plant size column (6-in diameter) would be required to show its overall potential in large water flow situations as an advanced stage of treatment following the conventional lime-neutralization, flocculation, and sedimentation treatment process. Many industries which discharge wastewaters containing heavy metals have installed or must install conventional lime-neutralization wastewater treatment

TABLE 24. PRELIMINARY JAR TESTS ON BRASS MILL WASTEWATER COMPARING VARIOUS ADDITIVES*

mg/1			Initial Cu	Final Cu	Final	%	Supernatant
ISX	Al^{3+}	Polymer†	μg/1	μg/1	pH	Reduction	at sampling
0	0	0	246	154	9.2	37.4	Clear
10	10.4	0	234	30	6.6	87.2	Clear
10	26.0	0	223	146	4.8	34.5	Clear
10	52.0	0	240	74	4.3	69.2	Clear
0	52.0	0	243	211	4.3	13.1	Clear
0	104.0	0	246	217	4.1	11.8	Clear
0	0	0	231	88	9.6	61.9	Clear
10	0	0	220	113	9.4	48.6	Clear
0	2.6	0	244	54	9.0	77.9	Clear
0	5.2	0	215	41	8.6	80.9	Clear
0	7.8	0	515	44	7.5	91.4	Clear
0	10.4	0	238	51	7.1	78.5	Clear
0	0	0	181	153	9.3	15.5	Clear
10	0	0	178	142	9.3	20.2	Clear
0	2.6	0	178	44	9.4	75.3	Clear
0	5.2	0	170	33	8.5	80.6	Clear
0	7.8	0	170	71	6.7	54.7	Clear
0	10.4	0	170	74	6.7	56.5	Clear
0	0	0	200	155	9.0	22.5	Clear
10	0	0	194	142	9.0	26.8	Clear
0	2.6	0	195	74	7.0	62.4	Clear
0	5.2	0	181	37	8.4	79.5	Clear
0	7.8	0	211	34	8.4	83.9	Some floc still suspended
0	10.4	0	184	32	8.4	82.9	Some floc still suspended
0	0	0	3,980	1,046	6.3	73.7	Clear
0	0	1.4	3,980	130	9.1	96.7	Best floc
0	0	1.4	3,980	800	6.4	79.9	Worse floc
0	10	1.4	3,980	492	5.7	87.6	Sl. turbid
0	10	0	3,980	561	5.7	85.9	Sl. turbid
0	10	1.4	3,980	92	9.1	97.8	Sl. turbid
0	10	0	3,980	92	9.1	97.8	Sl. turbid
10	0	1.4	3,980	103	9.1	97.4	Clear
10	0	1.4	3,980	561	6.6	85.9	Sl. turbid
10	10	1.4	3,980	271	5.5	93.2	Clear
10	10	0	3,980	400	5.5	89.9	Sl. turbid
10	10	1.4	3,980	35	9.1	99.1	Clear
10	10	0	3,980	40	9.0	99.0	Sl. turbid

* Samples (950 ml) were treated with the indicated additives and evaluated using standard jar test techniques. Samples were removed 3.2 cm below the surface after 10 min of settling.

† Olin 5002.

TABLE 25. PRELIMINARY JAR TESTS ON BRASS MILL WASTEWATER COMPARING VARIOUS ADDITIVES*

mg/1		Initial Cu	Final Cu	Final	%	
ISX	Al^{3+}	μg/1	μg/1	pH	Reduction	Comments
0	0	137	65	9.1	52.5	Clear
0	10	107	30	9.1	72.0	Clear
5	2.5	128	55	9.1	57.0	Very sl. turbid
5	5	121	50	9.1	41.3	Very sl. turbid
0	5	157	60	9.1	61.7	Very sl. turbid
5	10	114	37	9.1	67.5	Clear
0	0	206	82	9.1	60.2	Clear
5	5	212	9	9.0	95.7	Clear
0	10	227	12	9.0	94.7	Sl. floc suspended
10	5	241	9	9.0	96.3	Clear
5	10	214	5	9.0	98.1	Very sl. floc suspended
10	15	232	5	9.0	97.8	Very sl. floc suspended
0	0	276	95	9.1	65.6	Best
0	5	276	40	9.1	85.5	Best
0	10	286	40	9.0	86.0	Next best
0	20	490	45	9.0	90.8	Few flocs suspended
5	10	95	30	9.1	68.4	Few flocs suspended
15	10	110	26	9.1	76.3	Few flocs suspended

* Samples (950 ml) were treated with the indicated additives and evaluated using standard jar test techniques. Samples were removed 3.2 cm below the surface after 10 min of settling.

facilities to comply with the U.S. EPA Best Practical Treatment (BPT) guidelines. The most effective use of ISX with or without coagulants as an integral part of the conventional treatment process must be investigated further to determine whether or not the additional equipment and processes for advanced ISX treatment are necessary or economically reasonable.

LEAD BATTERY EFFLUENTS

Our major objective in treating the lead battery effluents we chose was to lower the lead concentration to less than 0.05 mg/1. One lead battery company (Indiana) wanted to reduce their residual lead concentration to less than 0.05 mg/1 and also to reduce their dissolved solids concentration so the water could be reused. During our bench-scale evaluations to reduce the lead concentration with ISX, we also considered dissolved solids removal. The other lead battery company (Pennsylvania) only desired lead removal to less than 0.05 mg/1 .

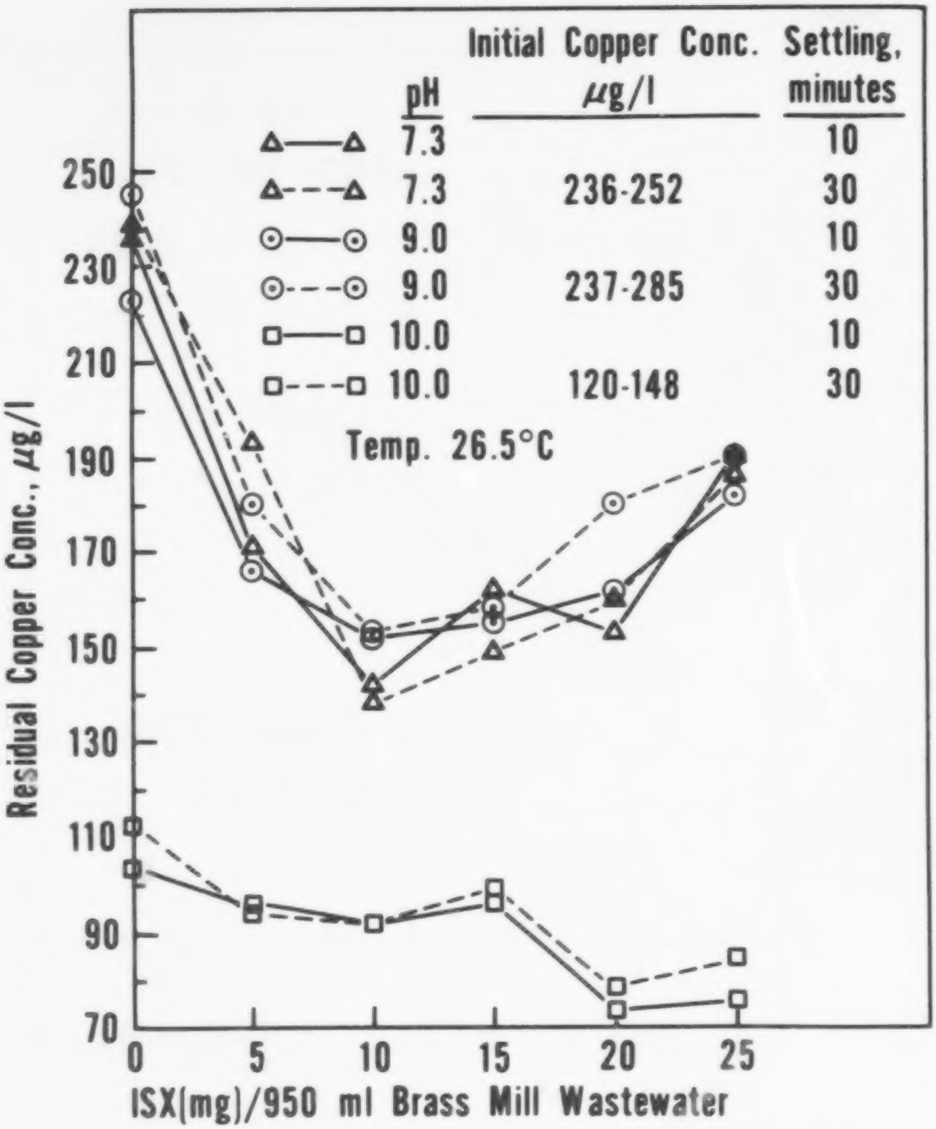


Figure 12. Treatment of brass mill wastewater with ISX only.

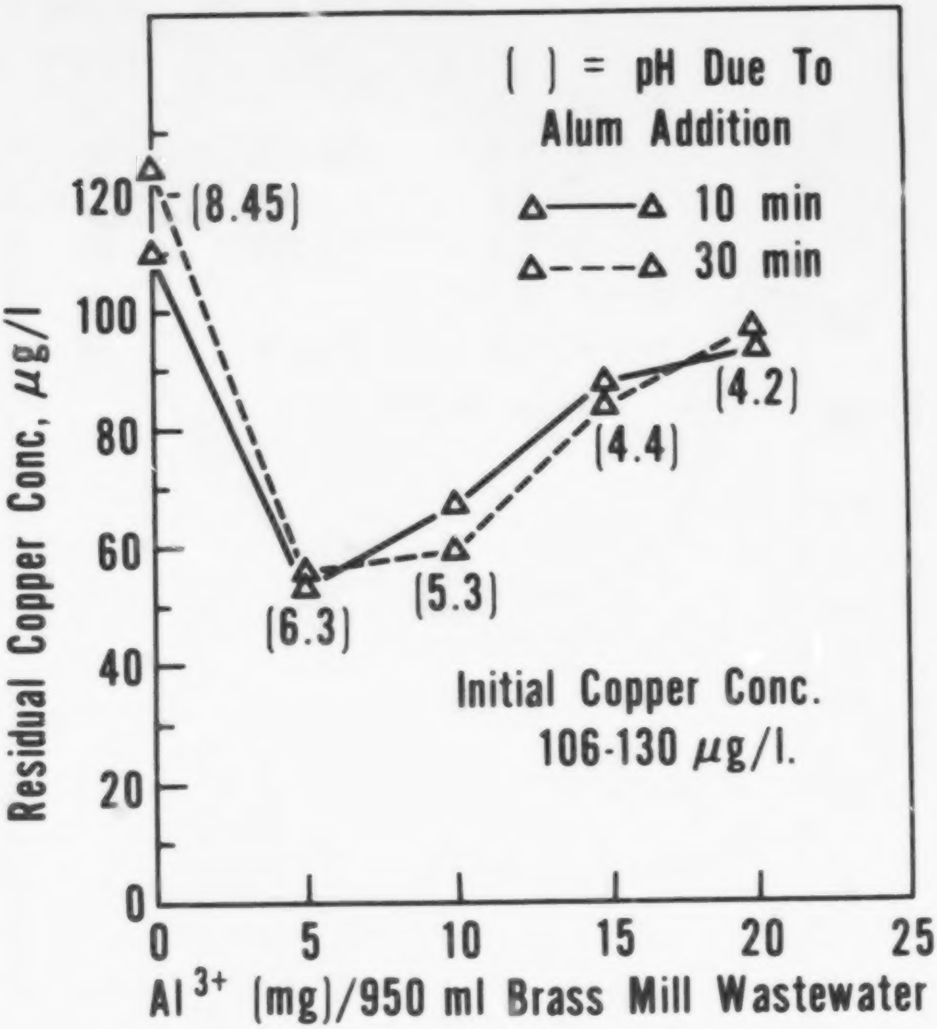


Figure 13. Treatment of brass mill wastewater with Al^{3+} only (no pH readjustment).

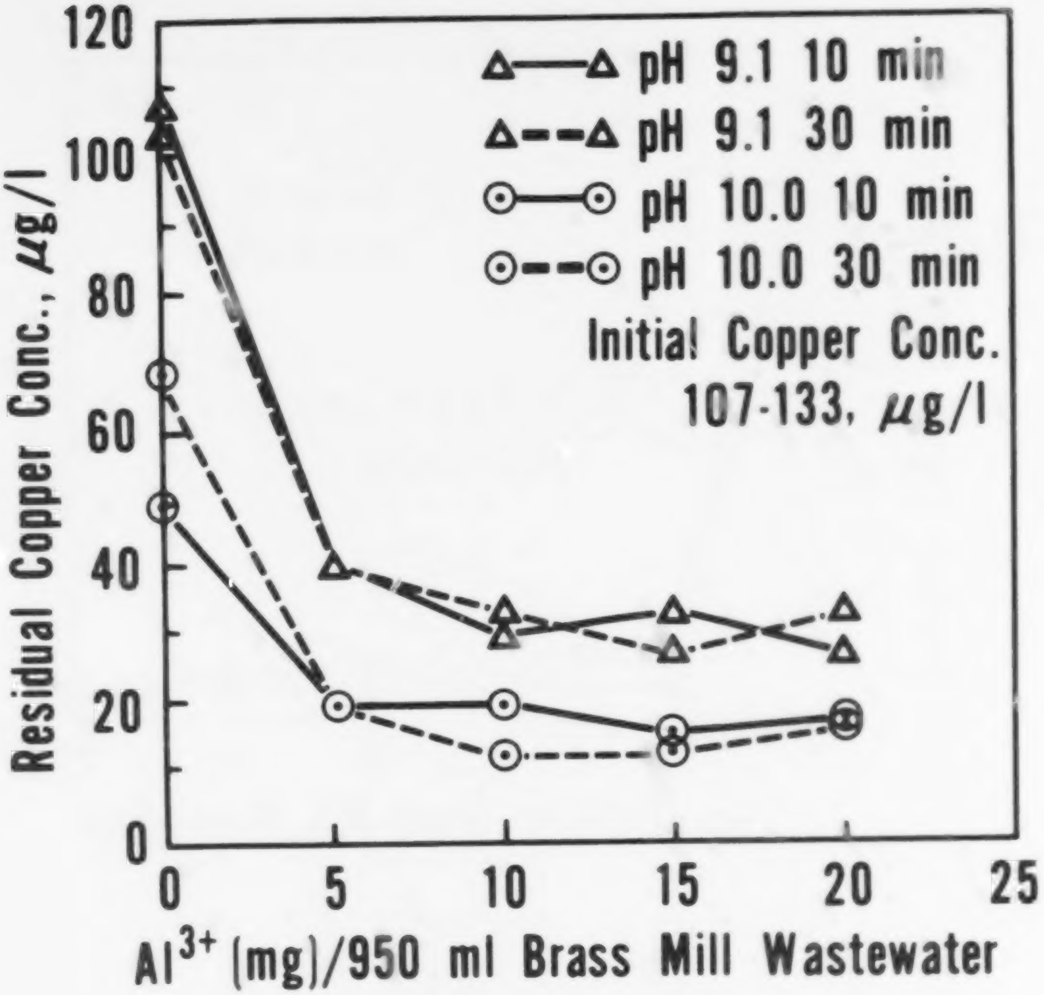


Figure 14. Treatment of brass mill wastewater with Al^{3+} only (pH readjustment).

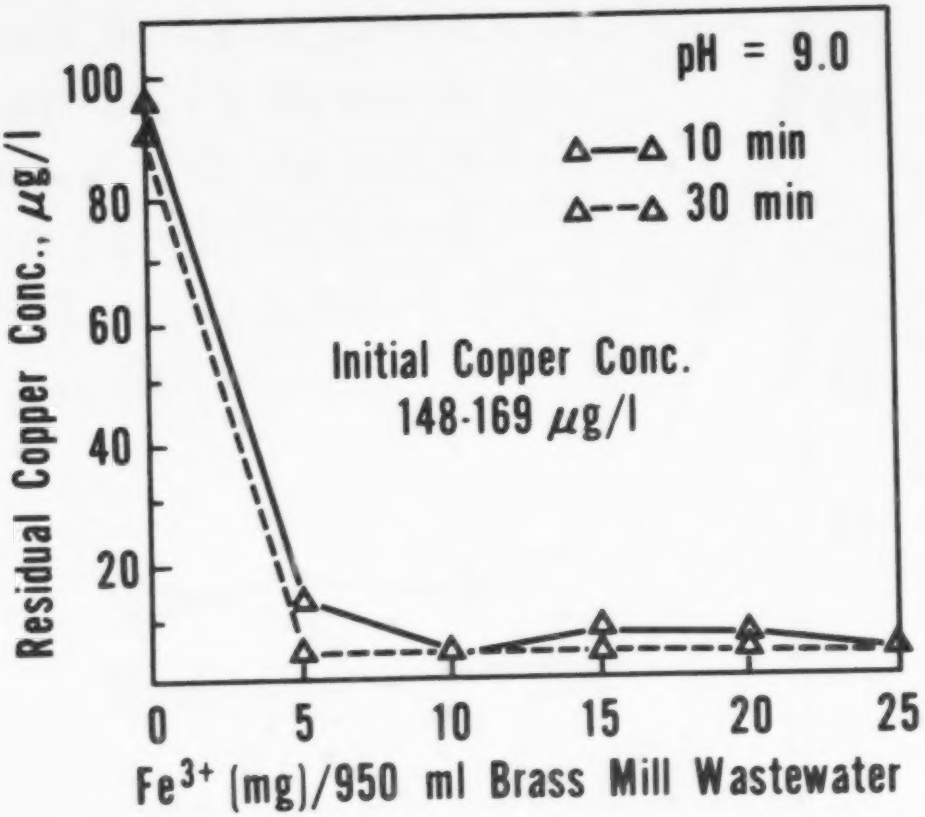


Figure 15. Treatment of brass mill wastewater with Fe^{3+} only.

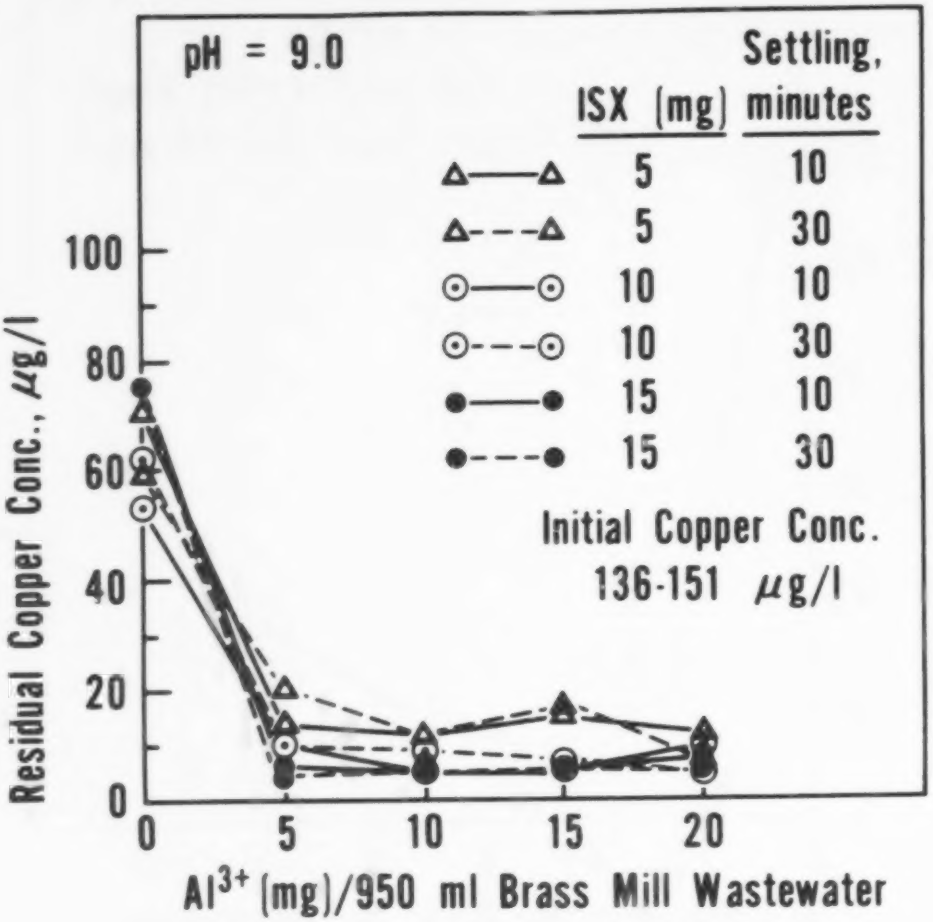


Figure 16. Treatment of brass mill wastewater with Al^{3+} and ISX.

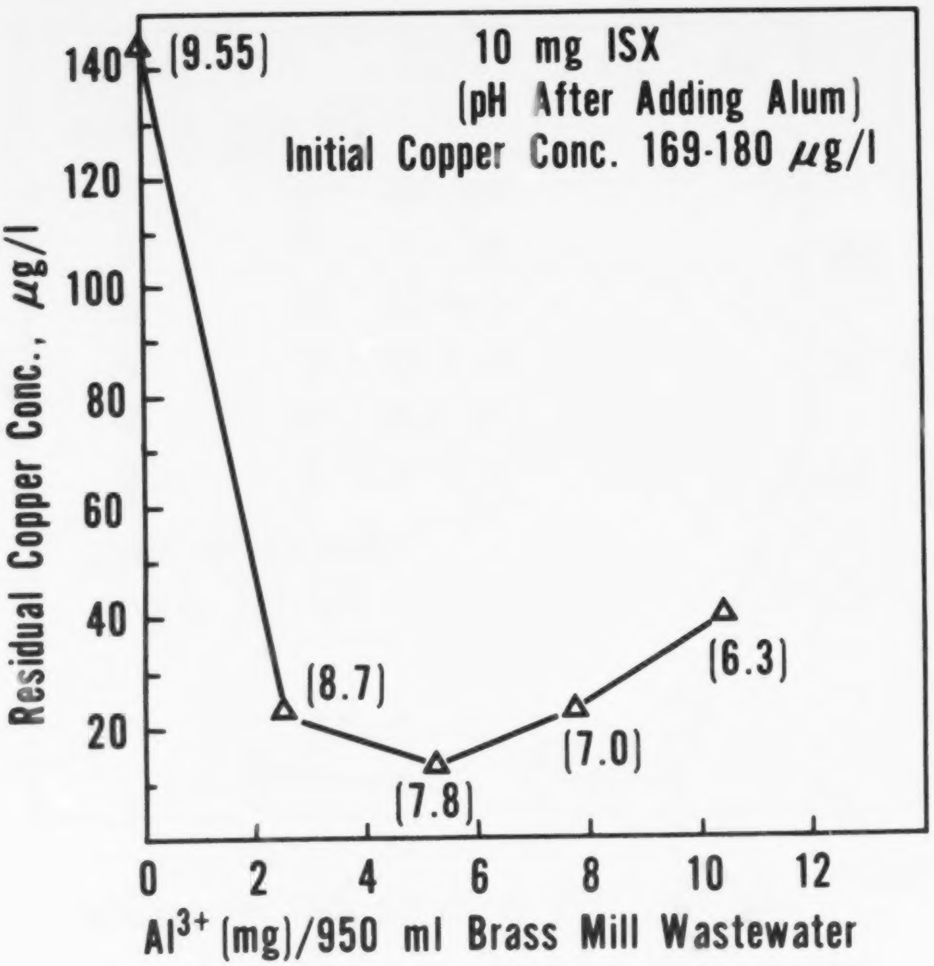


Figure 17. Treatment of brass mill wastewater with Al^{3+} and ISX (no pH readjustment).

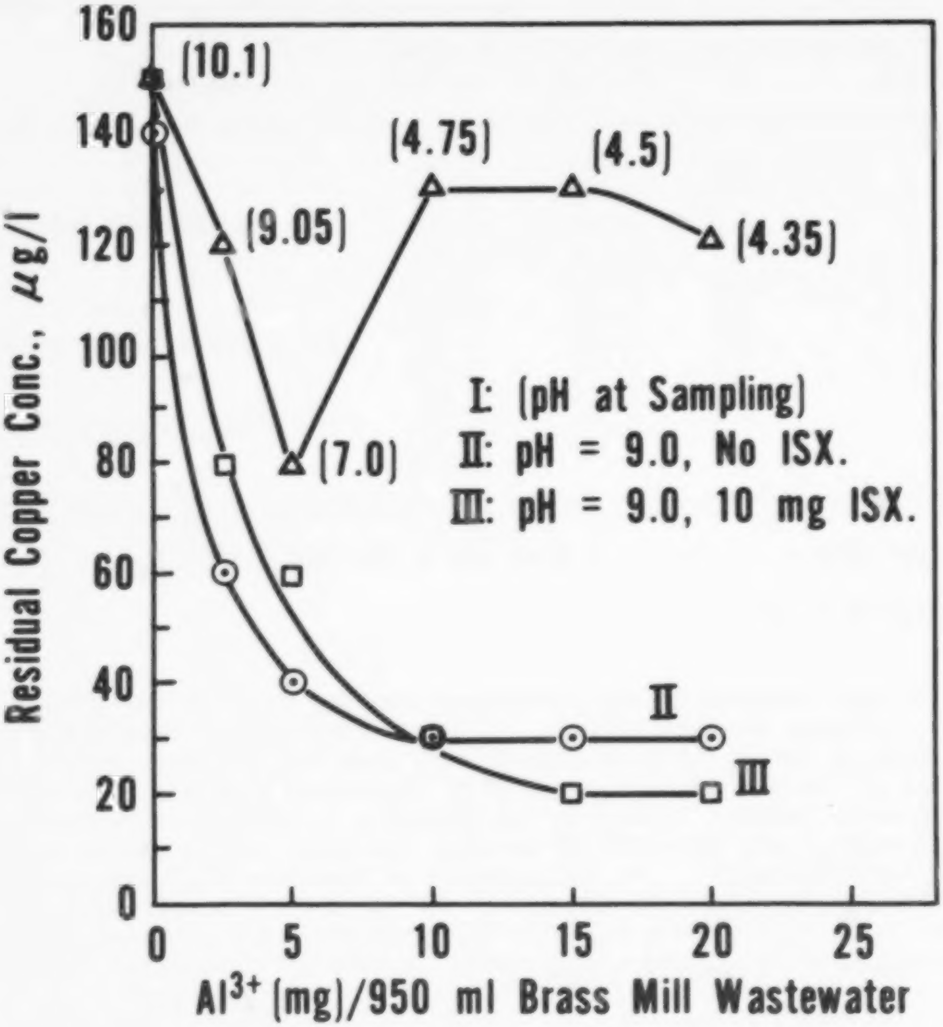


Figure 18. On-site jar tests at brass mill.

TABLE 26. CHEMICAL NEUTRALIZATION OF INDIANA LEAD BATTERY COMPANY EFFLUENT*

Neutralization Agent	Final pH	Residual Pb, mg/l	Residual Fe, mg/l	Comments
NaOH	5.0	0.233	1.04	
	7.0	0.287	0.934	
	8.0	0.209	0.625	2.7 g solid NaOH required
	9.0	0.186	0.625	
	10.0	0.175	0.166	
Na_2CO_3	7.0	0.268	0.487	
	8.0	0.311	0.068	6.3 g solid Na_2CO_3 required
	8.5	0.490	0.050	
$CaCO_3$	6.5†	0.189	5.89	
$Ca(OH)_2$	7.0	0.421	0.536	8.0 g solid $Ca(OH)_2$ required
	8.0	0.387	0.216	

* Initial [Pb] = 4.05 mg/l; Initial [Fe] = 52.0 mg/l; pH = 1.6.

† Maximum pH attainable.

The data obtained in the preliminary testing phase of the Indiana battery company effluent was very erratic. However, from general observations and the data shown in Tables 26-29 we were able to draw the following conclusions: (a) None of the neutralization agents by themselves gave any clear-cut advantage in metal removal. The order of settlability was very pronounced [$NaOH >> Ca(OH)_2 > Na_2CO_3$] and the order of residual dissolved solids was as expected $Ca(OH)_2 << Na(OH) < Na_2CO_3$. (b) ISX appeared to lower residual metal content. In these studies, however, the amounts of ISX added were insufficient to remove all the lead. (c) Soluble starch xanthate appeared to lower residual metal concentration slightly and significantly increased flocculation [$NaOH >> Ca(OH)_2 > Na_2CO_3$] of the sludge over using no flocculating agent. (d) Commercial anionic polyelectrolytes were very effective on increasing settling of the sludge [$NaOH >> Ca(OH)_2 > Na_2CO_3$]. (e) Barium carbonate was slightly effective in dissolved solids removal. Additional studies with barium hydroxide and calcium carbonate gave similar results.

The results (Tables 30-31) from the standard jar tests show that ISX does offer a way to reduce residual lead concentrations to below desired discharge limits. Our chemical treatments to reduce dissolved solids were very ineffective and ion-exhcange columns, reverse osmosis or distillation, would have to be used. Table 30 shows a 54-65% removal of lead with ISX. However, when sufficient ISX is incorporated as shown in Table 31, greater than 90% lead removal is noted with residual lead values below discharge limits.

TABLE 27. EFFECT OF CHEMICAL NEUTRALIZATION AND STARCH XANTHATES ON INDIANA LEAD BATTERY COMPANY EFFLUENT*

Neutralization agent	Additional treatment	Final pH	Residual Pb conc., mg/1	Residual Fe conc., mg/1	Dissolved solids g/1	Comments
NaOH	Soluble starch xanthate† (4 mg/1)	7.5	0.344	0.045	---	Good fast settling floc
NaOH	ISX‡ (0.05 g) then soluble starch xanthate (4 mg/1)	7.5	0.122	0.021	---	Good fast settling floc
NaOH	ISX (0.05 g) then Nalcolyte 676§ (4 mg/1)	7.5	0.311	0.026	---	Good fast settling floc
Na_2CO_3	Soluble starch xanthate (8 mg/1)	7.0	0.588	0.688	---	Slow settling floc
NaOH to pH 7.5 then $Ca(OH)_2$	Soluble starch xanthate (5 mg/1)	8.1	0.250	0.063	6.20	Good fast settling floc
$Ca(OH)_2$	Soluble starch xanthate (5 mg/1)	8.1	0.250	0.103	6.82	Medium settling floc

* Initial [Pb] = 4.05 mg/1; Initial [Fe] = 52.0 mg/1; pH = 1.6; dissolved solids = 4.94 g/1.

† Degree of substitution = 0.11 (5.07 g/1).

‡ 1.5 meq metal ion/g.

§ Commercial anionic polyelectrolyte.

TABLE 28. CHEMICAL NEUTRALIZATION AND ISX TREATMENTS FOR INDIANA LEAD BATTERY COMPANY EFFLUENT*

Treatment	Residual Pb conc., mg/1	Residual Fe conc., mg/1	Dried sludge,g	Dissolved solids, g/1	Comments
1. NaOH to pH = 4.0 2. Na_2CO_3 to pH = 8.5 3. Dow A-23† (2.5 mg/1)	0.158	<0.05	0.283	6.47	Slow settling in 5 min - good settling with polymer
1. NaOH to pH = 4.0 2. $Ca(OH)_2$ to pH = 8.5 3. Dow A-23 (2.5 mg/1)	0.125	<0.05	0.271	5.97	Medium settling in 5 min - good settling with polymer
1. NaOH to pH = 4.0 2. Na_2CO_3 to pH = 8.5 3. ISX‡ (0.1g) 4. Dow A-23 (2.5 mg/1)	0.121	<0.05	---	---	
1. NaOH to pH = 4.0 2. $Ca(OH)_2$ to pH = 8.5 3. ISX (0.1 g) 4. Dow A-23 (2.5 mg/1)	0.060	<0.05	---	---	

* Initial [Pb] = 4.05 mg/1; Initial [Fe] = 52.0 mg/1; pH = 1.6.

† Commercial anionic polyelectrolyte.

‡ 1.5 meq metal ion/g.

TABLE 29. BARIUM CARBONATE TREATMENT FOR DISSOLVED SOLIDS REDUCTION OF INDIANA LEAD BATTERY COMPANY EFFLUENT*

Neutralization agent	Additional treatment	Final pH	Residual Pb conc., mg/1	Residual Fe conc., mg/1	Dissolved solids g/1	Comments
NaOH	Soluble starch xanthate† 20 ml (10 mg/1)	7.0	---	---	6.09	Tight fast settling floc
Na_2CO_3	Soluble starch xanthate 20 ml (10 mg/1)	7.0	---	---	9.51	Slow settling floc
$Ca(OH)_2$	Soluble starch xanthate 20 ml (10 mg/1)	7.0	---	---	3.63	Loose medium settling floc
NaOH	0.3 g $BaCO_3$ then soluble starch xanthate 20 ml (10 mg/1)	9.4	0.100	0.050	5.24	
Na_2CO_3	0.3 g $BaCO_3$ then soluble starch xanthate 20 ml (10 mg/1)	7.7	0.200	0.085	8.95	
$Ca(OH)_2$	0.3 g $BaCO_3$ then soluble starch xanthate 20 ml (10 mg/1)	8.2	0.04	0.050	2.83	

* Initial dissolved solids - 4.94 g/1.

† Degree of substitution = 0.11 (5.07 g/1).

TABLE 30. STANDARD JAR TEST TREATMENTS* FOR INDIANA LEAD BATTERY COMPANY EFFLUENT

Experiment Number	1	2	3	4	5	6
Wastewater†, ml	950	950	950	950	950	950
Soluble starch xanthate‡, ml (mg/1)	0	8(4)	8(4)	0	8(4)	8(4)
Insoluble starch xanthate§, g (mg/1)	0	0	0.02 (20)	0	0	0.02 (20)
Water, ml	61.5	53.5	53.5	8	0	0
Initial pH	1.6	1.6	1.6	1.6	1.6	1.6
NaOH (7N), ml	9.5	9.5	9.5	0	0	0
Na_2CO_3 (10%), ml	0	0	0	63	63	63
Analysis after treatment						
Residual [Pb], mg/1	0.222	0.121	0.077	0.310	0.211	0.144
Residual [Fe], mg/1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Suspended solids, mg/1	39.3	42.6	19.5	67.8	81.1	75.9
COD, mg/1	104	---	80	96	---	140

* Jar tests were run according to published methods.

† Initial [Pb] = 4.05 mg/1, [Fe] = 52.0 mg/1.

‡ NRRC product-Degree of Substitution = 0.11.

§ NRRC product-Degree of Substitution = 0.20.

TABLE 31. STANDARD JAR TEST TREATMENTS* FOR INDIANA LEAD BATTERY COMPANY EFFLUENT

Sample Number	Treatments†	Residual Pb, mg/1‡	Residual Fe, mg/1‡	Sludge§ vol., ml	Dried# sludge, g	Dissolved** solids, g/1	Residual†† Pb, mg/1	Residual†† Fe, mg/1
1	NaOH (9.12 ml-2.55 g)	0.28	0.12	30	0.29	8.89	0.04	<0.05
2	$Ca(OH)_2$ (2.8 g)	0.31	0.11	45	1.44	9.09	0.03	<0.05
3	Na_2CO_3 (120 ml-12.0 g)	0.22	0.14	30	6.38	6.59	0.02	<0.05
4	NaOH (8.6 ml-2.40 g) to pH 5.0 then Na_2CO_3 (41.3 ml-4.13 g)	0.18	0.18	30	5.67	8.06	0.02	<0.05
5	NaOH (8.6 ml-2.40 g) to pH 5.0 then $Ca(OH)_2$ (0.20 g)	0.22	0.13	45	0.63	9.92	0.02	<0.05
6	NaOH (8.85 ml-2.49 g) to pH 6.0 then Na_2CO_3 (37.7 ml-3.77 g)	0.17	0.16	30	3.45	8.79	0.03	<0.05

* Jar tests were run according to published methods.

† Neutralization agents were added to 880 ml wastewater to pH 9.0. Water was added to bring all beakers to 1,000 ml. Magnifloc 837A (American Cyanamid) anionic polyelectrolyte (0.5 g/1, 2 ml) was added to flocculate the sludge.

‡ Residual metal concentrations were determined on a Varian Techtron AA 120 after filtration.

§ Apparent volume in bottom of 1-1 beakers.

# Weight of sludge after filtration and drying at 80°C for 24 hr.

** Dissolved solids in treated effluent.

†† The experiments were repeated incorporating 0.1 g/1 ISX before the flocculating agent.

The use of sodium carbonate in our opinion is not a good choice as a neutralization agent since it requires a large quantity to reach alkaline pH's. This results in additional dissolved solids which makes the water not recycleable unless treated further. The use of flocculating agents (anionic) offers a way to enhance sludge settling. Usually after 2 min the solids were completely settled. Soluble starch xanthate was evaluated to test its flocculating and metal removal ability. It was not as effective as commercial anionic polymers; however, its cost would be considerably less and it could be made on-site. Soluble starch xanthate by itself did show a 30-40% removal of lead.

Since the Pennsylvania battery effluent was already neutralized when received, we only evaluated ISX for lead removal in the presence of various anionic polyelectrolytes. The data in Tables 32-34 show that ISX does remove lead from this wastewater. In Table 32, the ISX (0.02 g) was an insufficient amount to do an effective job. This table also shows that a soluble starch xanthate of a higher degree of substitution (D.S.) is not as effective as one with a lower D.S. Commercial anionic polymers because of their higher molecular weight are superior flocculants. Table 33 shows that increasing the ISX concentration does lower the lead concentration further. In this study, we also evaluated a new insoluble carboxylated crosslinked starch and this product also was found to be effective in lead removal. The data in Table 34 show ISX in sufficient amount will reduce the lead concentration to below the desired 0.05 mg/l limit when it is added before flocculation. Some lead removal is observed after sludge removal; however, we feel that this residual amount remaining could be as a colloidal lead hydroxide for which ISX would have no affinity.

Battery companies have a choice of neutralization agents to adjust their wastewater to alkaline pH's. We feel a combination of NaOH to pH 4-6 and then $Ca(OH)_2$ or Na_2CO_3 to 8.5 offers some advantages in dissolved solids removal, sludge amount, and flocculation ability. The use of ISX for lead removal to below 0.05 mg/l is a way to meet their discharge limit. We also feel it is advantageous to add the ISX before the anionic polymer.

CIRCUIT BOARD RINSE WATERS

We were contacted by several printed circuit board manufacturers to evaluate ISX in copper removal from several different rinse waters. During our investigation, we found ISX was only partially effective when copper was in a complexed form [very effective though for $Cu(NH_3)_4^{2+}$]. Therefore, we carried out investigations further to develop simple, economical processes which were effective in complexed copper removal. The rinse waters causing the most problems to these companies were from (a) electroless copper, (b) copper pyrophosphate, and (c) copper etching operations. The following discussion presents our findings into the ways these copper complexes can be removed from industrial effluents.

Copper Removal from Electroless Copper Plating Rinse Waters

The normal operating pH of electroless copper baths is in the range of 12-13. In this pH range, the copper complex is soluble when calcium ion is not

TABLE 32. STANDARD JAR TEST TREATMENTS* FOR PENNSYLVANIA LEAD BATTERY COMPANY EFFLUENT

Experiment Number	1	2	3	4	5	6
Wastewater,† ml	960	960	960	960	960	960
Soluble starch xanthate,‡ ml	0	8	8	8§	8§	0
ISX,# g	0	0	0.02	0	0.02	0
Nalco 676** (0.5 g/1), ml	0	0	0	0	0	4
Water, ml	40	32	32	32	32	36
Analysis after treatment						
Residual [Pb], mg/1	1.03	0.87	0.67	0.82	0.67	0.88
Comments	slow settling	good settling	good settling	slow settling	slow settling	fast settling

* Jar tests were run according to published methods.

† Initial [Pb] = 1.03 mg/1, pH = 10.6.

‡ NRRC product - degree of substitution = 0.11 (5.07 g/1).

§ NRRC product - degree of substitution = 0.35 (5.07 g/1).

# NRRC product - 1.50 meq metal ion/g.

** Commercial anionic polyelectrolyte.

TABLE 33. STANDARD JAR TEST TREATMENTS* FOR PENNSYLVANIA LEAD BATTERY COMPANY EFFLUENT

Experiment Number	1	2	3	4	5	6
Wastewater,† ml	960	960	960	960	960	960
Soluble starch xanthate,‡ ml (mg/1)	0	20(10)	8(4)	0	0	0
ISX,§ g (mg/1)	0	0	0.05 (50)	0.05(50)	0	0
Carboxylated starch,# g (mg/1)	0	0	0	0	0.05(50)	0.10(100)
Water, ml	40	20	32	40	40	40
Analysis after treatment						
Residual Pb, mg/1	1.05	0.162	0.108	0.091	0.076	0.059

* Jar tests were run according to published methods.

† Initial [Pb] = 10.3 mg/1, pH = 10.6.

‡ NRRC product - degree of substitution = 0.11 (5.07 g/1).

§ NRRC product - 1.50 meq metal ion/g.

# NRRC product - 2.92 meq metal ion/g.

TABLE 34. ISX ADDITIONS BEFORE AND AFTER FLOCCULATION OF PENNSYLVANIA LEAD BATTERY COMPANY EFFLUENT

	Sample* size, ml	ISX,† g	Dow-A23,‡ mg/l	Residual Pb, mg/l	Dried§ sludge, g
Before	1,000	0.1	2.5	0.045	6.33
After	1,000	0.1	2.5	0.112 (0.167)#	7.76

* Initial [Pb] = 1.03 mg/l, pH 10.6.

† NRRC product - 1.50 meq metal ion/g.

‡ Commercial anionic polyelectrolyte.

§ Sludge was filtered off and dried for 24 hr at 110°C.

# Lead conc. after polyelectrolyte addition.

TABLE 35. LOG FORMATION CONSTANTS FOR COMPLEXES AT pH 12 (52-55)

Ions	Ligands		
	EDTA	HEDTA	NTA
Ca^{2+}	10.7	8.4	6.5
Cu^{2+}	15.7	13.7	12.0
Δ log K Ca^{2+}-Cu^{2+}	5.0	5.3	5.5

present. Treatment of copper complexes of the EDTA type with calcium hydroxide at a pH greater than 11.5 yields a copper hydroxide precipitate. The formation of this precipitate might be unexpected since the copper-EDTA stability constant at pH 11-12 is 10^5 times greater than the constant for the calcium-EDTA complex (52-55) (Table 35). However, if one considers the formation constants and solubility product constants for the species involved [Cu^{2+}, Ca^{2+}, $EDTA^{4-}$, and $Cu(OH)_2$] one would expect to get copper removal (Table 36). The removal of copper from several different types of complexes by calcium ion over a limited pH range is an effective treatment for rinse waters of the electroless plating of copper.

TABLE 36. EQUILIBRIUM CONCENTRATIONS FOR Cu^{2+}-Ca^{2+}-$EDTA^{4-}$ SYSTEM AT pH 12

	Conditions			
Species*	Case I†	Case II‡	Case III§	Case IV#
Cu^{2+}	1.0×10^{-15}	6.0×10^{-16}	1.2×10^{-5}	6.0×10^{-16}
$CuEDTA^{2-}$	6.0×10^{-4}	5.4×10^{-4}	5.9×10^{-4}	1.7×10^{-13}
$EDTA^{4-}$	1.2×10^{-4}	1.8×10^{-4}	**	**
Ca^{2+}	---	---	2575×10^{-4}	2570×10^{-4}
$CaEDTA^{2-}$	---	---	1.3×10^{-4}	7.2×10^{-4}
$Cu(OH)_2$	---	0.6×10^{-4} (10%)	---	6.0×10^{-4} (100%)

* Concentrations in moles/l.

† Excess of EDTA with large formation constant for $CuEDTA^{2-}$ ignoring possibility of $Cu(OH)_2$.

‡ Excess of EDTA with large formation constant for $CuEDTA^{2-}$ considering precipitation of $Cu(OH)_2$.

§ Concentrations of Cu^{2+}, Ca^{2+}, and $EDTA^{4-}$ ignoring solubility limit of $Cu(OH)_2$.

# Concentrations of Cu^{2+}, Ca^{2+}, and $EDTA^{4-}$ considering solubility limit of $Cu(OH)_2$).

** Completely complexed due to excess metal ions.

Copper-EDTA Complex--

Several variables in the treatment process were evaluated to determine what effect calcium ion had on the decomposition of the copper-EDTA complex. Tables 37 and 38 present several treatments which show that excess calcium ion (>150 mg/l) at a pH of 11.6 or greater will reduce copper levels to 0.2 mg/l or less. Table 37 shows that effective copper removal can be achieved with Ca^{2+}/Cu^{2+} ratios greater than 2.5 above pH 11.7. Even though there was a slight increase in pH over these various addition levels, it was actually the increase in calcium ion which caused the decrease in the residual copper. At a pH lower than 11.5 with sufficient calcium ion in solution (270 mg/l), no precipitation was observed. As the pH was raised with the addition of more calcium hydroxide or sodium hydroxide to a pH of 11.6 or greater, the copper precipitates (99.6% removal) as the hydroxide. Good removal is obtained over a pH range of 11.6 to 13.5; however, the optimum precipitation of copper hydroxide from a copper-EDTA complex is in the pH range of 11.6 to 12.5 (Table 37).

TABLE 37. COPPER REMOVAL FROM COPPER-EDTA COMPLEX--DETERMINATION OF AMOUNT OF CALCIUM ION REQUIRED* AND EFFECT OF pH†

$Ca(OH)_2$ Added, g	Ca^{2+}/Cu^{2+}	Final pH	Residual copper‡ conc., mg/l
Calcium ion required			
0.05	0.54	11.7	28.67
0.10	1.08	11.8	5.17
0.15	1.62	11.9	2.01
0.20	2.16	12.0	1.05
0.25	2.70	12.1	0.82
0.50	5.41	12.2	0.23
Effect of pH			
0.5		11.5	50.0
0.5		11.7	0.18
0.5		12.0	0.39
0.5		12.5	0.46
0.5		13.0	1.65
0.5		13.5	3.75

* Dilute 26.18 ml copper-EDTA stock solution to 1 l (50 mg Cu/l) and then adjust to pH 11.7 with sodium hydroxide (1N). Treat with calcium hydroxide for 5 min, add Nalcolyte 676 (1.5 mg/l), and allow to settle 15 min before filtering.

† Follow * using initial pH 10.9 with 0.5 g calcium hydroxide. All pH adjustments above 11.5 were made with sodium hydroxide.

‡ Determined using Varian Techtron AA 120 spectrophotometer.

Rinse solutions containing 50 mg/l complexed copper at temperatures of 20-60°C were treated with $Ca(OH)_2$ (0.50 g/l) to a pH of 11.7. Dilute NaOH was used to correct minor pH changes. Residual copper concentrations were in the range of 0.29-0.50 mg/l.

Apparently most calcium compounds are effective as long as they are soluble above pH 11.5. Calcium hydroxide (1.85 g/l, 0°C), calcium oxide (1.31 g/l, 10°C), calcium chloride (5.95 g/l, 0°C), and calcium sulfate (2.09 g/l, 30°C) all are soluble to give good removal (Table 38). However, calcium carbonate (0.0153 g/l, 25°C) is too insoluble to give effective copper removal. Other calcium salts were not evaluated because they offered no economical or ecological advantage.

TABLE 38. COPPER REMOVAL FROM COPPER-EDTA COMPLEX--EFFECT OF CALCIUM SALT AND COPPER CONCENTRATION*

Stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
26.18	50	10.9	CaO	0.50	11.6	1.5	0.14
26.18	50	10.9	$CaCl_2$	0.75	11.6‡	1.5	0.22
26.18	50	11.7‡	$CaCl_2$	0.75	11.6	1.5	0.20
26.18	50	10.9	$CaSO_4$	0.92	11.7‡	1.5	0.44
26.18	50	10.9	$CaCO_3$	0.68	11.6	1.5	36.00
26.18	50	3.3§	$Ca(OH)_2$	0.69	11.7	1.5	0.05
26.18	50	10.9	$Ca(OH)_2$	0.50	11.7	1.5	0.18
26.18	50	10.9	$Ca(OH)_2$	0.50	11.7	---	1.21#
2.62	5	10.3	$Ca(OH)_2$	0.50	11.6	1.5	0.10
52.36	100	11.1	$Ca(OH)_2$	1.00	11.6	1.5	0.09
250**	1,910	11.7	$Ca(OH)_2$	1.29	12.0	1.5	3.40

* One-liter solutions were prepared from the volume of stock indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

§ pH adjusted with H_2SO_4 (1N).

# Filtered after 16-hr settling.

** Used without dilution.

When calcium chloride and calcium sulfate are used, a slight pH lowering is observed due to copper hydroxide precipitation from solution. When calcium oxide and calcium sulfate are used, an excess of calcium is noted in the sludge due to their limited solubility at this pH. The described treatment is effective on dilute rinses (5-100 mg/l) and even concentrated baths (1,910 mg/l) (Table 38).

The copper hydroxide floc which forms will gravity settle over a 4-16 hr period. The supernatant of these treated rinses usually contained a concentration in excess of 1 mg/l residual copper (Table 38). These higher copper values could result from a copper $\rightleftharpoons$ copper hydroxide equilibrium which exists in these systems or from some small colloidal particles of copper hydroxide which passed through the filter. However, if an anionic polyelectrolyte is added such as Nalcolyte 676 or Dow Purifloc A-23 (1.5 mg/l), the copper hydroxide sludge settles quite rapidly and can be removed before an equilibrium can develop. If the sludge is removed in less than 4 hr, no increase in dissolved copper concentration is observed. Probably most anionic polyelectrolytes would be effective flocculants for this treatment system.

Analysis of the blue sludge after dissolution in acid (5% HCl) and subsequent reprecipitation at pH 6-7 with sodium hydroxide indicated pure copper hydroxide. A nitrogen analysis of the sludge was negative, which proved the EDTA was in solution probably as the calcium complex. Evaporation of the solution followed by nitrogen analysis of the resulting solid showed all the EDTA to be here. Excess calcium ion could be removed from the treated water by carbon dioxide treatment to form insoluble calcium carbonate.

Copper-NTA Complex--

Copper removal (99.9%) utilizing this calcium ion treatment from a copper-NTA complex is very similar to that of EDTA (Table 39). The variables discussed for EDTA also apply for the copper-NTA complex. Additional $NTA \cdot Na_3$ (0.0065 moles/l) had to be used over EDTA to form a stable complex.

Copper-HEDTA Complex--

When complexes are used containing hydroxyl groups in place of acetate, the copper removal (97%) is somewhat less effective (Table 40). Since calcium does not bind as effectively with hydroxyl groups as with acetate, copper removal might be expected not to be as complete (53).

Copper-NDA Complex--

The calcium ion treatment is only 95% effective in the decomposition of the copper-NDA complex. Even though the copper hydroxide precipitates from solution, floc formation is poor under normal treatment conditions even with an excess of anionic polyelectrolyte. However, at a pH of 12 with an excess of calcium ion, a better floc is formed (Table 41).

TABLE 39. COPPER REMOVAL FROM COPPER-NTA COMPLEX*

Stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
28.60	50	11.0	CaO	0.50	11.6	1.5	0.22
28.60	50	11.0	$CaCl_2$	0.75	11.7‡	1.5	0.35
28.60	50	11.0	$CaSO_4$	0.92	12.0‡	1.5	0.44
28.60	50	11.0	$Ca(OH)_2$	0.50	11.7	1.5	0.06
2.86	5	10.1	$Ca(OH)_2$	0.34	11.7	1.5	1.39
57.20	100	11.1	$Ca(OH)_2$	0.40	11.7	1.5	0.60
250§	1,730	11.8	$Ca(OH)_2$	1.00	12.0	2.0	8.1
250§	1,730	11.8	$CaCl_2$	1.27	11.7	2.0	21.05
250§	1,730	11.8	$CaCl_2$	1.82	11.7	2.0	3.8

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (IV).

§ Used without dilution.

TABLE 40. COPPER REMOVAL FROM COPPER-HEDTA COMPLEX*

Stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
26.5	50	10.8	CaO	0.50	11.7	1.5	5.42
26.5	50	10.8	$CaCl_2$	0.75	11.8‡	1.5	1.30
26.5	50	10.8	$CaSO_4$	0.92	11.8‡	1.5	6.96
26.5	50	10.8	$Ca(OH)_2$	0.50	11.8	1.5	1.73
2.65	5	9.6	$Ca(OH)_2$	0.50	11.8	1.5	0.61
53.0	100	11.1	$Ca(OH)_2$	0.50	11.8	1.5	12.59
250§	1,890	11.8	$Ca(OH)_2$	2.00	12.0	2.0	36.62

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

§ Used without dilution.

TABLE 41. COPPER REMOVAL FROM COPPER-NDA COMPLEX*

Stock solution, ml	Initial copper conc., mg/l	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/l	Residual† copper conc., mg/l
27.93	50	11.0	CaO	0.50	11.7	4.5	4.60
27.93	50	11.0	$CaCl_2$	0.75	11.8‡	4.5	2.30
27.93	50	11.0	$Ca(OH)_2$	0.50	11.7	4.5	2.86
2.79	5	10.4	$Ca(OH)_2$	0.50	11.8	4.5	0.24
55.86	100	11.5	$Ca(OH)_2$	0.50	11.8	4.5	26.90
250§	1,790	11.8	$CaCl_2$	2.00	11.7	6.0	326

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

§ Used without dilution.

Copper-Tartrate Complex--

Treatment of dilute copper-tartrate complexes with calcium ion at pH 11.6 or greater is only 60-85% effective (Table 42). The use of excess calcium ion, treatment to higher pH values (>12.0) and longer stirring times increase copper removal. Since calcium tartrate is fairly insoluble (0.032 g/l, 0°C), a considerable amount of the tartrate is also precipitated by the calcium ion treatment. This fact has been proven by chemical analysis of the sludge. Dissolution of the sludge in acid (5% HCl) and reprecipitation with sodium hydroxide precipitates some copper hydroxide at pH 6-7; however, it takes a pH of 10 to reprecipitate the rest of the copper and calcium tartrate. The copper-tartrate complex is the only one tested where the complexing agent is partially precipitated during calcium ion treatment.

Copper-Citrate Complex--

Treatment of dilute copper-citrate solutions with calcium ion gives similar results to tartrate (Table 43); however, the calcium-citrate complex is more soluble (8.5 g/l, 18°C) and remains in solution. Excess calcium ion and higher pH (>12.0) appear to aid in copper removal. However, when calcium chloride is added at pH 11.2, a good copper hydroxide floc is formed. The calcium ion treatment was totally ineffective in removal of copper from the concentrated copper-citrate bath. The copper-citrate baths that were synthetically prepared were only stable for a few hours, after which time pure copper was autocatalytically deposited on the sides of the container.

Calcium-Gluconate Complex--

Even though gluconate forms a similar type of complex to citrate or tartrate, two differences were noted. Treatment of the gluconate complexes appear to give better copper removal at lower pH (10.9-11.6), and if very dilute solutions (5 mg/l copper) are treated there is no apparent removal (Table 44). Calcium gluconate is very soluble (21.1 g/l, 15°C) and all the gluconate remained in solution as the calcium salt.

Copper-Triethanol and Copper-Quadrol Complexes--

Treatment of these complexes at several pH's with different calcium salts gave no copper removal.

Commercial Copper Complexes--

Table 45 shows the excellent removal (99.9%) from a commercial EDTA-type bath (MacDermid A). This bath was received at a pH 2.5 to prevent any spontaneous autocatalytic decomposition during transit. The acid treatment did not affect copper removal by calcium ion. Several other complexes of copper were evaluated (Table 46). Shipley solution A, which is probably a citrate-type complex, is only partially decomposed by calcium ion. Treatment of Shipley A rinse solutions gave 50-80% copper removal; however, no removal is observed when the stock solution is treated. Rinse solutions of MacDermid B and Shipley B, C, and D are completely stable to calcium ion treatment at high pH.

TABLE 42. COPPER REMOVAL FROM COPPER-TARTRATE COMPLEX*

Stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
46.0	50	11.0	CaO	0.50	11.7	1.5	19.38
46.0	50	11.0	$CaCl_2$	0.75	12.3‡	1.5	7.17
46.0	50	11.0	$CaSO_4$	0.92	11.9‡	1.5	20.27
46.0	50	11.0	$Ca(OH)_2$	0.50	11.9	1.5	21.00
46.0	50	12.0‡	$Ca(OH)_2$	0.50	12.3	1.5	13.48
46.0	50	3.3§	$Ca(OH)_2$	1.00	11.5	1.5	10.70
46.0	50	11.0	$Ca(OH)_2$	1.00#	11.6	1.5	6.39
4.6	5	10.5	$Ca(OH)_2$	0.50	12.0	1.5	0.88
92	100	11.5	$Ca(OH)_2$	1.00	12.3	2.0	8.45
250**	1,082	12.0	$Ca(OH)_2$	2.00	12.1	2.0	6.05
250**	1,082	12.0	$CaCl_2$	2.00	11.9	2.0	19.20

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

§ pH adjusted with H_2SO_4 (1N).

Used a 30-min stirring time.

** Used without dilution.

TABLE 43. COPPER REMOVAL FROM COPPER-CITRATE COMPLEX*

Stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
44.56	50	11.0	CaO	0.50	12.1	1.5	21.98
44.56	50	11.0	$CaCl_2$	0.75	11.2	1.5	32.78
44.56	50	11.0	$CaCl_2$	0.75	12.0‡	1.5	26.48
44.56	50	11.0	$Ca(OH)_2$	0.50	11.8	1.5	21.00
44.56	50	11.0	$Ca(OH)_2$	0.50	12.1‡	1.5	9.01
44.56	50	11.0	$Ca(OH)_2$	1.0	12.1	1.5	11.63
4.46	5	10.5	$Ca(OH)_2$	0.5	11.8	1.5	1.26
89.12	100	11.4	$Ca(OH)_2$	1.0	12.0	1.5	45.86

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

TABLE 44. COPPER REMOVAL FROM COPPER-GLUCONATE COMPLEX*

Stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
32.23	50	10.9	CaO	0.50	11.8	1.5	22.09
32.23	50	11.0	$CaCl_2$	0.75	10.9	1.5	15.89
32.23	50	11.0	$CaSO_4$	0.92	11.8‡	1.5	22.91
32.23	50	10.9	$Ca(OH)_2$	0.50	11.5	1.5	23.83
32.23	50	11.0	$Ca(OH)_2$	0.50	12.1‡	1.5	26.20
3.22	5	10.4	$Ca(OH)_2$	0.34	11.8	1.5	5.00
64.46	100	11.2	$Ca(OH)_2$	0.22	11.7	1.5	24.61
250§	1,551	11.9	$CaCl_2$	1.00	11.8	2.0	160.30
250§	1,551	11.8	$CaCl_2$	2.00	11.7	2.0	129.40

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

§ Used without dilution.

TABLE 45. COPPER REMOVAL FROM A COMMERCIAL COPPER-EDTA-TYPE COMPLEX*

MacDermid A stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
15	53.85	3.5	CaO	0.67	11.8	1.5	0.18
15	53.85	3.5	$CaCl_2$	0.75	11.7†	1.5	0.22
15	53.85	3.5	$Ca(OH)_2$	0.42	11.6	1.5	0.26
15	53.85	3.5	$Ca(OH)_2$	1.00	11.6	1.5	0.02
15	53.85	3.5	$Ca(OH)_2$	1.00	11.6	---	0.20§
13.92	50	10.9‡	$Ca(OH)_2$	0.46	11.7	1.5	0.32
13.92	50	10.9‡	$Ca(OH)_2$	0.46	11.7	---	1.20#
2	7.37	4.1	$Ca(OH)_2$	1.00	11.7	1.5	0.06
100	356.7	2.9	$Ca(OH)_2$	1.20	11.6	2.0	0.87
500**	3,566	2.5	$Ca(OH)_2$	3.68	11.6	2.0	21.67

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

§ Filtered without polymer treatment after 15-min settling.

# Filtered after 16-hr settling.

** Used without dilution.

TABLE 46. COPPER REMOVAL FROM OTHER COMMERCIAL COPPER COMPLEXES*

No.	Stock solution, ml	Initial copper conc., mg/1	Initial pH	Calcium salt	Weight of salt, g	Final pH	Polymer conc., mg/1	Residual† copper conc., mg/1
Shipley								
A	17.73	50	11.0	CaO	0.50	12.0	1.5	23.07
A	17.73	50	10.9	$CaCl_2$	0.75	10.9	1.5	24.08
A	17.73	50	10.9	$CaCl_2$	0.75	12.3‡	1.5	9.00
A	17.73	50	10.9	$CaSO_4$	0.92	11.9‡	1.5	1.62
A	17.73	50	11.0	$Ca(OH)_2$	0.48	11.7	1.5	12.00
A	35.46	100	11.2	$Ca(OH)_2$	0.50	11.9	1.5	50.50
A	250§	2,820	12.0	$Ca(OH)_2$	2.00	12.3	---	2,820
A	250§	2,820	12.0	$CaCl_2$	2.00	12.0	---	2,820
MacDermid								
B	44	50	10.2	$Ca(OH)_2$	1.00	11.8	---	50
Shipley								
B	10.33	50	10.9	$Ca(OH)_2$	0.77	11.7	---	50
C	18.05	50	11.2	$Ca(OH)_2$	0.37	11.8	---	50
D	13.62	50	10.9	$Ca(OH)_2$	0.82	11.7	---	50

* One-liter solutions were prepared from the volume of stock solution indicated and were treated accordingly.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ pH adjusted with NaOH (1N).

§ Used without dilution.

The results show that treatment of electroless copper rinses or baths is not always effective with calcium ion at high pH. The chemical structure of the complexing agents in most cases determines which solutions will be decomposed. If the nitrogen in the complexing agents is completely substituted with carboxyl groups, removal of copper by calcium ion is almost complete. In most cases, copper removal is greatly reduced if complexing agents are used which have some of the carboxyl groups replaced by hydrogen or hydroxyl groups. Complexing agents containing no carboxyl groups and only hydroxyl groups show no copper removal.

Some of the excess of calcium required for these treatments probably precipitates as calcium carbonate, since carbonate is known to be present in these types of rinse waters. This calcium ion treatment at high pH can be conducted batchwise and probably could be operated continuously; however, only batchwise treatment has been evaluated. Since the major product in the proposed treatment is copper hydroxide (except when tartrate is the complexing agent), the sludge could be reprocessed to recover copper in a reusable form to help defray cost of treatment. Chemical cost of treatment for a 50 mg/l copper-EDTA rinse with lime and polymer would be about $0.08/1,000 gal. The supernatant after treatment would still contain a calcium complex but it would have a much lower toxicity. Care should be taken in discharge of the calcium complex effluent since the complexing agent will combine with other heavy metal ions when the pH is lowered. Several recent reports (56-58) do show that copper in a complex form, i.e., with EDTA, NTA, or pyrophosphate, is significantly less toxic than free copper ion. Formate, a byproduct of formaldehyde catalyzed electroless copper baths, does not interfere with copper removal in this proposed treatment and would remain soluble as calcium formate (16.2 g/l, 0°C). The addition of small amounts of sulfide ion, ISX, or dithiocarbamates after the calcium ion treatment aids in further copper removal.

An industrial electroless plating rinse was evaluated containing copper (173 mg/l) and nickel (51.9 mg/l) as the tartrate complex. After treatment with calcium ion, the residual copper was 0.3 mg/l and the nickel was 0.1 mg/l. These results were unexpected since treatment of standard copper tartrate complexes only resulted in 60-80% copper removal. These results were reported to the company and after similar success in their laboratory, the decision was made to install hardware for this high pH-lime treatment process (January, 1977 start-up). They had evaluated at considerable expense RO, electrochemical, low pH-lime, sodium borohydride, and other techniques. They were using sodium borohydride reduction until the more economical and more effective high pH-lime treatment was installed. Presently they use a premixed lime-calcium chloride slurry to have a higher calcium ion concentration and they modify the amounts daily depending on their copper-nickel concentrations. Their electroless copper rinse water (40,000 l/day) initially contains copper (50-300 mg/l) and nickel (0-150 mg.l) and after high pH-lime treatment to pH 11.5-12.0, the residual concentrations are 0.04-0.3 mg.l copper and 0.03-1.0 mg/l nickel, which satisfys the river discharge limit of 1.0 mg/l for each metal. The sludge is hauled away to an approved landfill.

ISX was evaluated for copper removal from these complexes; however, the copper removal was not very effective unless the pH of the solution was lowered to a pH of 3-5 to where the copper complex dissociates. Since the calcium ion treatment offered a more economical approach, the use of ISX was not evaluated further.

Since several commercial baths were untreatable by the calcium ion method, we expanded our investigations to develop an effective treatment process for these types of copper complexes. Chemical suppliers told us that the complexing agent was Quadrol (Figure 1).

We discovered that if rinse waters containing this type of copper complex were lowered to pH's where the complex dissociates, ferrous sulfate added and the solution neutralized to a pH above 9, effective copper removal was obtained. This treatment is effective because the ferrous ion reduces the Cu^{2+} to Cu^{+} and when the pH is raised, the copper will not recomplex. Acidification was used in most of the studies because it assists in weakening or dissociating the bonds in the copper complex and this is evidenced by a color change in the solution from pale blue to colorless. The color change is a useful guide to the amount of acid required for the pH adjustment and if companies have rinses that turn colorless, acid would only have to be added to that pH. In most of our studies we lowered the pH to 2.7. Even though the data of Table 47 suggest the best treatment would be the addition of ferrous sulfate to the rinse with no prior acidification, we found that some of the commercial rinses known to be of the Quadrol-type gave better treatment by lowering the pH to 2.7. These commercial rinses were the ones that did not turn colorless at low pH's.

Table 47 also shows that as the copper concentration of the rinse increases, the Fe^{2+}/Cu^{2+} ratio can be lowered from 8.0 to 1.0 for effective treatment. This fact is especially important from an economic point of view. Since companies are going more to counterflow rinsing techniques for water use reduction, the copper complex concentration will increase, so this more effective utilization of ferrous sulfate will be realized. The use of calcium hydroxide and sodium hydroxide as neutralization agents (Table 47) were equally effective in copper and iron removal; however, the use of sodium hydroxide gave lower dissolved solids and less sludge. The amount of ferrous sulfate and the use of sodium hydroxide vs calcium hydroxide were also determined for the MacDermid B rinse and the results were similar to those just discussed for copper-Quadrol. The contact time at low pH with ferrous sulfate for 1 hr or a stir at pH 11.2 for 2 hr after ferrous sulfate treatment showed no improvement in metal removal and in fact at longer contact at 11.2 the residual copper and iron increased. As long as the pH is raised above 9.0 (Table 48) the copper removal is excellent, however, to lower the residual iron to low values the pH had to be raised to 11.7.

Since we desired residual copper concentrations less than 0.05 mg/l we chose to use 1.0 g/l ferrous sulfate for 50 mg/l copper solutions and 0.4 g/l ferrous sulfate for 10 mg/l copper solutions. Companies could use considerably less ferrous sulfate if these lower copper values were not required. The ferrous sulfate treatment was evaluated on solutions containing different synthetic copper complexes (Table 49). Whereas the previously discussed calcium treatment was only very effective for the EDTA-type copper complexes, the

TABLE 47. COPPER REMOVAL FROM COPPER-QUADROL COMPLEX--DETERMINATION OF AMOUNT OF FERROUS SULFATE REQUIRED AND EFFECT OF BASE*

Copper conc., mg/1	Adjusted pH	$FeSO_4 \cdot 7H_2O$, g	Fe^{2+}/Cu^{2+}	Base	Residual copper conc.,† mg/1	Residual iron conc.,† mg/1
50	2.7	0.3	1.2	$Ca(OH)_2$	33.0	4.74
50	2.7	0.4	1.6	$Ca(OH)_2$	15.5	8.70
50	2.7	0.5	2.0	$Ca(OH)_2$	0.58	9.46
50	2.7	0.75	3.0	$Ca(OH)_2$	0.16	5.68
50	2.7	1.0	4.0	$Ca(OH)_2$	0.01	2.68
50	2.7	0.5	2.0	NaOH	1.25	8.42
50	2.7	0.75	3.0	NaOH	0.22	4.54
50	2.7	1.0	4.0	NaOH	0.05	5.16
50	9.5‡	0.5	2.0	$Ca(OH)_2$	0.44	6.38
50	7.8	0.75	3.0	$Ca(OH)_2$	0.01	6.70
50	7.2	1.00	4.0	$Ca(OH)_2$	0.01	7.41
50	7.2§	1.00	4.0	$Ca(OH)_2$	0.09	3.06
10	2.7	0.20	4.0	$Ca(OH)_2$	6.60	0.49
10	2.7	0.30	6.0	$Ca(OH)_2$	1.42	1.52
10	2.7	0.40	8.0	$Ca(OH)_2$	0.07	1.00
10	5.4‡	0.20	4.0	$Ca(OH)_2$	1.00	1.48
1000	2.7	3.0	0.6	$Ca(OH)_2$	421.0	27.5
1000	2.7	4.0	0.8	$Ca(OH)_2$	147.0	85.0
1000	2.7	5.0	1.0	$Ca(OH)_2$	0.36	12.5

* Copper-Quadrol solutions (1,000 ml) containing the indicated copper concentration at pH 10.6-11.9 were acidified with 1N H_2SO_4 to pH 2.7. Ferrous sulfate was added as a solid and after 5 min, the pH was raised to 11.2 with the base listed. Nalcolyte 676 (2.5 mg/1) anionic polyelectrolyte was added and the solutions were allowed to settle 5 min before filtering.

† Determined using a Varian Techtron AA 120 spectrophotometer.

‡ No acid added, pH lowering due to ferrous sulfate addition.

§ Solution lowered to pH 2.7 after ferrous sulfate addition.

TABLE 48. EFFECT OF FINAL pH* ON COPPER REMOVAL FROM COPPER-QUADROL COMPLEX

Adjusted pH	Final pH	Residual copper conc.,† mg/l	Residual iron conc.,† mg/l
2.7	7.0	0.24	25.4
2.7	9.0	0.17	10.5
2.7	11.0	0.14	4.5
2.7	11.7	0.05	0.31
6.4‡	7.0	1.34	48.6
6.4‡	9.0	0.01	13.8
6.4‡	11.0	0.01	1.4
6.4‡	11.7	0.01	0.23
9.0§	9.0	0.01	14.1
9.0§	11.0	0.01	1.9
9.0§	11.7	0.01	0.17

* Dilute 39.0 ml copper-Quadrol stock solution to 1 l (50 mg Cu/l) and then adjust the solutions to the desired pH with 1N H_2SO_4. Treat solutions with ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 1.0 g) for 5 min, add calcium hydroxide to the indicated pH and add Nalcolyte 676 (2.5 mg/l) for flocculation. After settling 5 min, an aliquot (10 ml) was filtered through Whatman 54 filter paper for analysis.

† Copper and iron concentrations were determined using a Varian Techtron AA 120 spectrophotometer.

‡ Adjusted to pH 7.0 with acid, then to pH 6.4 with ferrous sulfate.

§ Adjusted to pH 9.0 with ferrous sulfate.

ferrous sulfate treatment was effective on all the complexes evaluated. Commercial rinses containing various copper complexes were treated with ferrous sulfate with excellent copper removal (Table 50).

The effluent after treatment in most cases was clear and colorless. When the iron concentration was high in some experiments, the effluent was pale yellow and sometimes hazy. This was overcome as previously mentioned by adjustment of the solution to a higher pH (11.7). The use of anionic polyelectrolytes (1.0-2.5 mg/l) was very effective in the flocculation and settling of the sludge. Samples allowed to settle for 16 hr had residual copper concentrations above 1 mg/l whereas with the polyelectrolyte flocculated samples the residual copper concentration was consistantly below 0.1 mg/l when the sludge

TABLE 49. COPPER REMOVAL FROM SYNTHETIC COPPER COMPLEXES WITH FERROUS SULFATE TREATMENT*

Complex	Initial copper conc., mg/1	2N H_2SO_4, ml	pH for colorless† solution	$FeSO_4 \cdot 7H_2O$, g	$Ca(OH)_2$, g	Residual copper conc., mg/1	Residual iron conc., mg/1
EDTA	50	3.8		1.0	1.16	0.23	0.12
	10	0.8		0.4	0.94	0.28	0.10
NTA	50	2.2		1.0	1.26	0.29	0.11
	10	0.7		0.4	0.44	0.09	0.11
Tartrate	50	8.0	4.5-4.8	1.0	1.54	0.75	0.21
	10	2.0		0.4	0.64	0.35	0.29
Gluconate	50	2.5	4.5-4.7	1.0	0.88	0.82	32.70
	10	0.7		0.4	0.53	0.09	6.20
Citrate	50	4.8	4.0	1.0	0.76	0.01	0.28
	10	1.8		0.4	0.45	0.02	0.18
Triethanol Amine	50	6.0	5.5	1.0	1.04	0.11	24.48
	10	1.5		0.4	0.64	0.53	8.33
Quadrol	50	5.9	3.0	1.0	0.73	0.01	2.68
	10	1.3		0.4	0.51	0.07	1.00

* Solutions (1,000 ml) containing the copper complexes at the indicated concentrations were acidified with 2N H_2SO_4 to pH 2.7. The indicated amount of ferrous sulfate was added and the solution stirred for 5 min. Calcium hydroxide was added to raise the pH to 11.7 and the solutions were flocculated with Nalcolyte 676 (2.5 mg/1) anionic polymer. After settling the solutions were filtered for analysis.

† pH values listed is where copper complex dissociates. When no value is listed, the blue complex does not dissociate above pH 1.8.

TABLE 50. COPPER REMOVAL FROM COMMERCIAL COPPER COMPLEXES WITH FERROUS SULFATE TREATMENT*

Bath	Initial copper conc., mg/1	$2NH_2SO_4$, ml	pH for colorless† solution	$FeSO_4 \cdot 7H_2O$, g	$Ca(OH)_2$, g	Residual copper conc., mg/1	Residual iron conc., mg/1	Dissolved‡ solids, mg/1
MacDermid								
A	50	---		1.0	1.42	0.02	7.1	---
A	10	---		0.4	0.46	0.02	2.3	---
B	50	15.0	2.7-3.0	1.0	1.69	0.17	17.8	---
B	10	4.7		0.4	0.50	0.08	6.3	---
C	50	19.0		1.0	2.18	0.09	21.0	---
C	10	6.0		0.4	0.60	0.03	5.9	---
Shipley								
A	50	4.0	4.8	1.0	0.56	0.33	0.53	---
A	10	1.6		0.4	0.27	0.21	0.47	---
B	50	4.5	2.8	1.0	0.61	0.27	24.86	---
B	10	1.1		0.4	0.26	0.31	2.78	---
C	50	8.2	3.9	1.0	0.94	0.20	14.17	---
C	10	1.8		0.4	0.27	0.11	2.72	---
D	50	3.5	3.8	1.0	0.51	0.12	6.94	1,750
D	10	1.7		0.4	0.34	0.20	1.47	720
D	50	---		---	---	---	---	817
D	50	3.5		1.0	0.92	0.08	6.85	2,320
D	50	3.5		1.0	20.5 ml§	0.16	8.88	2,064

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* Solutions (1,000 ml) containing the copper complexes at the indicated concentrations were acidified with 2N H_2SO_4 to pH 2.7. The indicated amount of ferrous sulfate was added and the solution stirred for 5 min. Calcium hydroxide was added to raise the pH to 11.7 and the solutions were flocculated with Nalcolyte 676 (2.5 mg/1) anionic polymer. After settling the solutions were filtered for analysis.

† pH values listed is where copper complex dissociates. When no value is listed, the blue complex does not dissociate above pH 1.8.

‡ Filtered samples were evaporated to dryness, oven dried at 125°C, cooled, and weighed.

§ Sodium hydroxide (1N).

was removed within an hour. The same results were also observed with the residual iron concentration. The sludge produced in this treatment was usually greenish-brown and very filterable. Several treatments using sodium hydroxide as the neutralization agent yielded a sludge that was very magnetic. Even though we only evaluated the treatment batchwise, it could be operated continuously metering in ferrous sulfate solutions. The chemical cost of treatment for a 50 mg/l copper-Quadrol type rinse with sulfuric acid, ferrous sulfate, lime, and polymer would be about $0.36/1,000 gal.

Copper Removal From Copper Pyrophosphate Rinse Waters--

It is well known that cations such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, and Fe^{3+} form insoluble precipitates with $HPO_4{}^{2-}$ and $P_2O_7{}^{4-}$ when an excess of cation is present (59-67). Since calcium hydroxide, lime, and calcium chloride are economical sources of Ca^{2+}, they were chosen for this study. As the Ca^{2+} is added to the rinse, it complexes with the $HPO_4{}^{2-}$ and the excess $P_2O_7{}^{4-}$ precipitating them as their insoluble calcium salts. When the excess $P_2O_7{}^{4-}$ is removed, the copper precipitates probably as $Cu_2P_2O_7$.

The copper pyrophosphate baths and rinses evaluated for the proposed treatment process were from the printed circuit industry which uses these baths for through-hole-plating of printed circuit boards. Since occasional analysis (68-69) for copper, pyrophosphate, orthophosphate, and ammonia is required for control purposes to keep the bath in good operating condition, the plater knows the relative concentrations of pyrophosphate and orthophosphate in his rinses. Using this analytical information, we designed a treatment process to lower the copper and phosphorus concentrations of synthetic and actual rinse waters. The proposed treatment process can be modified as the orthophosphate concentration builds up. New baths will contain very little orthophosphate, and treatment of rinse waters from these baths with calcium hydroxide or lime at pH's above 9 will give excellent copper and phosphorus removal. As the orthophosphate concentration builds up to >90 g/l, the substitution of some calcium chloride for lime will be required to get more Ca^{2+} into solution for excellent precipitation.

Synthetic solutions of known Cu^{2+}, $P_2O_7{}^{4-}$, and $HPO_4{}^{2-}$ concentrations were used to determine the optimum amounts of Ca^{2+} as $Ca(OH)_2$, lime, or $Ca(OH)_2$-$CaCl_2$ mixtures to be added to lower the total copper concentration to less than 0.02 mg/l and total phosphorus concentration to less than 1 mg/l. All calcium compounds were added as solids. Table 51 shows that when an excess of Ca^{2+} is present, a pH of 9-11.5 maximizes removal of copper. The pH's usually fell in this range with the amount of lime or calcium hydroxide added. Calculations performed from the data presented in Table 52 and Figure 19 show that 2.7 mmoles Ca^{2+} are required to remove 0.9 mmoles $P_2O_7{}^{4-}$ and 2.0 mmoles Ca^{2+} are required to remove 1.0 mmoles $HPO_4{}^{2-}$. From this information it is possible to calculate the amount of Ca^{2+} required for any amount of $P_2O_7{}^{4-}$ and $HPO_4{}^{2-}$ in actual rinse solutions.

Table 53 shows the composition of some actual baths. Even though the $P_2O_7{}^{4-}/Cu^{2+}$ ratio is somewhat high and the $HPO_4{}^{2-}$ concentration of Bath C is well out of the preferred operation range, the above described Ca^{2+} ratios were used to treat diluted samples from these baths. The results in Tables 54 and

TABLE 51. EFFECT OF pH ON COPPER AND PYROPHOSPHATE REMOVAL*

Final pH	Residual Cu, mg/1	Residual P, mg/1
5.6	7.14	4.3
7	1.38	2.2
8	0.14	1.6
9	0.01	0.2
10	0.01	0.2
11	0.01	0.2
11.5	0.02	0.2

* Copper pyrophosphate solutions (500 ml, containing 22.87 mg total copper and 157.3 mg total pyrophosphate) were treated with 525 mg calcium chloride (190 mg calcium ion) to a pH of 5.6. Dilute sodium hydroxide was used to adjust the solutions to the indicated pH. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/1) was added and the residual copper and phosphorus concentrations were determined after filtration.

55 show that the calculated Ca^{2+} ratio is applicable. Tables 54 and 55 also show treatment results for some diluted dragout rinses from these baths. Since $Ca(OH)_2$ has a limited water solubility, a combined $Ca(OH)_2$-$CaCl_2$ treatment was used for data in Table 55. The $Ca(OH)_2$ weight was calculated for the total $P_2O_7^{4-}$ present and the $CaCl_2$ weight for the HPO_4^{2-} present in the rinse. Since actual rinses may vary from 10 to 100 mg/1 Cu^{2+} having corresponding $P_2O_7^{4-}$ and HPO_4^{2-} concentrations, Ca^{2+} treatments were performed on rinses with concentrations in this range and the data are shown in Table 54.

Since the actual composition of the sludge in precipitating the $P_2O_7^{4-}$ and HPO_4^{2-} was not determined and because of the low residual Ca^{2+} concentrations in the treated rinses, an insoluble complex such as $Ca_5(OH)(PO_4)_3$ (59, 60, 65) is possible. This would also account for the excess amount of Ca^{2+} required.

It is assumed that the copper precipitates as $Cu_2P_2O_7$. This assumption has been proven by varying the pH of precipitated pure copper pyrophosphate solutions. In the pH range of 3-9, this precipitate is light blue in color; however, above pH 10 the precipitate becomes royal blue. This coloring is also true in treatment of actual rinses. If the copper precipitated as the

TABLE 52. COPPER REMOVAL FROM PURE COPPER PYROPHOSPHATE SOLUTIONS*

Sample	$Ca(OH)_2$, mg	Ca^{2+}, mg	Residual Cu, mg/1	Residual P, mg/1
1	150	81	9.55	---
2	175	95	3.60	---
3	200	108	0.02	0.2
4	250	135	0.01	0.2
5	300	162	0.01	0.2

* Copper pyrophosphate solutions (500 ml, containing 22.87 mg total copper and 157.3 mg total pyrophosphate) at initial pH's of 9.1 were treated with various amounts of calcium hydroxide to final pH's of 10.6-11.4. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/1) was added and the residual copper and phosphorus concentrations were determined after filtration.

TABLE 53. ACTUAL COPPER PYROPHOSPHATE BATH COMPOSITION

Components	Bath A oz/gal	Bath A g/1	Bath B oz/gal	Bath B g/1	Bath C oz/gal	Bath C g/1
Cu^{2+}	2.6	19.49	2.5	18.74	2.9	21.74
$P_2O_7{}^{4-}$	24.3	182.17	22.9	171.67	29.8	223.40
$HPO_4{}^{2-}$	1.5	11.25	11.6	84.96	22.3	167.17
NH_3	0.28	2.10	0.48	3.60	0.68	5.10
Ratio $P_2O_7{}^{4-}/Cu^{2+}$	9.3/1		9.2/1		10.3/1	
pH	8.95		8.15		8.15	

hydroxide, this color change would not be observed and the $Cu(OH)_2$ would dissolve at pH's less than 5.

If desired, the residual Ca^{2+} in the treated rinse could be removed by carbonation with carbon dioxide, which would give a concomitant lowering of pH. If this carbonation is performed the pH of the effluent should not be lowered below 9 if the phosphate sludge is still present. It is recommended, if the rinse to be treated requires more than 1.3 g/1 $Ca(OH)_2$, that some $CaCl_2$ be used for greater Ca^{2+} solubility. Even though the described treatment was

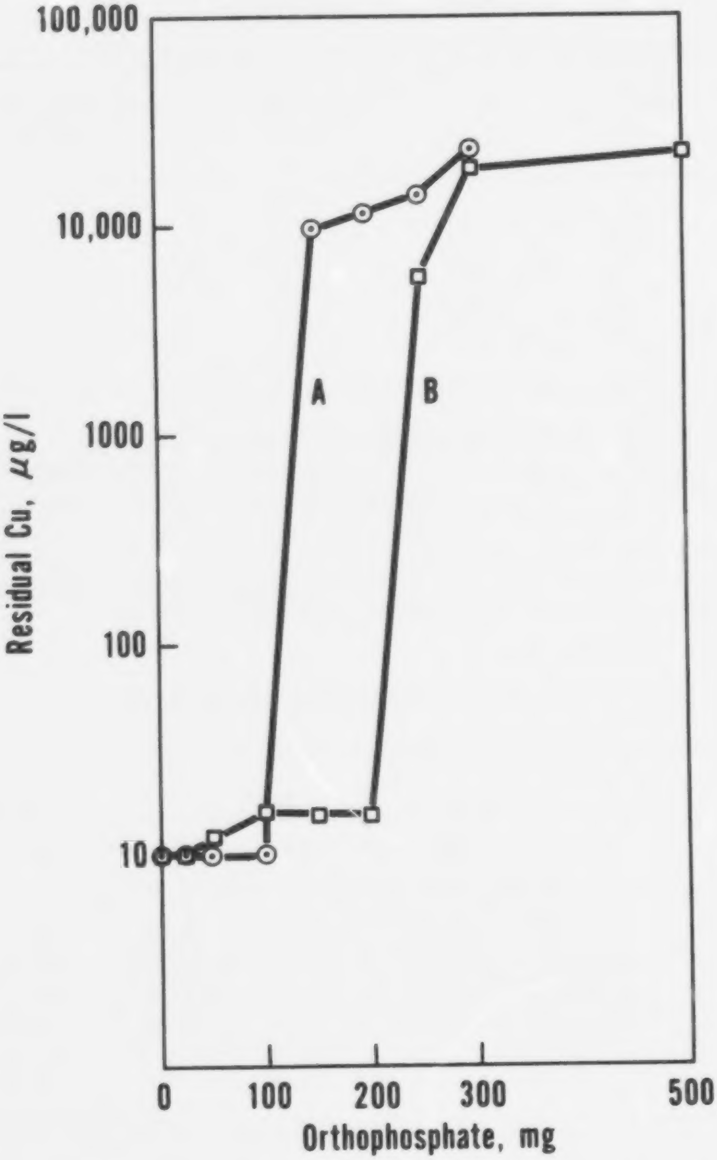

Figure 19. Copper removal from copper pyrophosphate with calcium ion vs increasing orthophosphate concentration.

Copper pyrophosphate solutions (500 ml, containing 22.87 mg total copper and 157.3 mg total pyrophosphate) containing the indicated amounts of orthophosphate were treated with calcium hydroxide (A, 350 mg-190 mg as Ca^{2+}; B, 500 mg-270 mg as Ca^{2+}) to a final pH of 11.2-11.6. After stirring 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/1) was added and after filtration the residual copper concentration was determined on a Varian Techtron AA 120.

TABLE 54. $Ca(OH)_2$ TREATMENT OF ACTUAL COPPER PYROPHOSPHATE ELECTROPLATING RINSES*

Rinse	Initial Cu conc., mg/1	Initial pH	Initial $P_2O_7^{4-}$ conc., mg/1	Initial HPO_4^{2-} conc., mg/1	$Ca(OH)_2$, mg	Residual Cu conc., mg/1	Residual P conc., mg/1	Residual Ca conc., mg/1	Final pH
A	67.36	8.9	728.7	45.0	992	0.02	0.2	30.2	11.4
B	74.50	8.1	686.7	347.8	1,387	0.04	0.6	14.3	11.5
C	70.84	7.7	893.6	668.7	2,124	2.54	3.1	3.6	11.4
A	50	8.6	539	33.4	734	0.02	0.2	27.4	11.1
B	50	8.0	460	233	929	0.01	0.2	19.7	11.2
C	50	7.7	625	468	1,487	0.02	0.2	44.7	11.3
A	10	8.4	108	6.7	147	0.01	0.2	---	10.6
B	10	8.1	92	47	186	0.01	0.2	---	10.8
A	100	8.7	1,078	67	1,470	0.02	0.2	---	11.6
B	100	8.1	920	466	1,860	0.02	0.2	---	11.6
A	50	8.6	539	33.4	550 (as lime)	0.01	0.2	---	11.1

* Copper pyrophosphate rinse solutions (1,000 ml) containing the indicated concentration were treated with calcium hydroxide. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/1) was added and residual copper, calcium, and phosphorous were determined after filtration.

TABLE 55. $Ca(OH)_2$-$CaCl_2$ TREATMENT OF ACTUAL COPPER PYROPHOSPHATE ELECTROPLATING RINSES*

Rinse	Initial Cu conc., mg/1	Initial pH	Initial $P_2O_7^{4-}$ conc., mg/1	Initial HPO_4^{2-} conc., mg/1	$Ca(OH)_2$, mg	$CaCl_2$ mg	Residual Cu conc., mg/1	Residual P conc., mg/1	Residual Ca conc., mg/1	Final pH
A	67.36	8.9	728.7	45.0	925	97	0.02	0.3	25.4	11.4
B	74.50	8.1	686.7	347.8	872	751	0.01	0.2	10.2	11.4
C	70.84	7.7	893.6	668.7	1,135	1,444	0.01	0.2	37.2	11.1
A	50	8.6	539	33.4	685	72	0.02	0.2	16.1	11.2
B	50	8.0	460	233	584	503	0.01	0.2	16.7	11.1
C	50	7.7	625	468	794	1,011	0.02	0.2	31.5	11.1

* Copper pyrophosphate rinse solutions (1,000 ml) containing the indicated concentration were treated with calcium hydroxide and calcium chloride. After stirring for 5 min, anionic polyelectrolyte (Dow A-23, 5 mg/1) was added and residual copper, calcium, and phosphorous were determined after filtration.

only evaluated batchwise, it could probably be operated continuously by using a slurry or solution of the calcium compound. The precipitate settles fairly rapidly; however, settling can be accelerated with the addition of 3-5 mg/l of an anionic polyelectrolyte. The chemical cost of treatment for a copper pyrophosphate rinse using lime and polymer containing Cu^{2+} (54 mg/l), total $P_2O_7^{4-}$ (500 mg/l) and HPO_4^{2-} (250 mg/l) would be about $0.16/1,000 gal.

Actual on-site treatments have been successful with Fe^{3+} substituted for some of the Ca^{2+}. During our investigation with concentrated copper pyrophosphate baths, preliminary results show that if large concentrations of copper sulfate solutions are added to these baths the excess pyrophosphate complexes with this copper to form a precipitate along with the copper pyrophosphate in solution and some copper orthophosphate. The HPO_4^{2-} remaining in solution can then be removed with excess Ca^{2+}.

Copper Removal from Copper Etchant Rinse Waters--

Rinses from ammonium persulfate etching operations are acidic; however, raising the pH with caustic does not remove all the $Cu(NH_3)_4^{2+}$ complex unless steam is used to drive off the ammonia so copper hydroxide can precipitate. The same is true of alkaline etch rinse waters. ISX was evaluated (Figure 20) on several synthetic and industrial rinses and the copper concentration was lowered from 28-54 mg/l to less than 0.1 mg/l. Chemical analysis (%N) of the sludge showed that the whole $Cu(NH_3)_4^{2+}$ complex is removed, which is an added advantage (ammonia removal). A 1-hr ISX contact time aided the complex removal in some cases. Several of the ammonium persulfate etches contain small concentrations of mercuric chloride to increase the etch rate and ISX has already been shown to be effective on this pollutant (Hg^{2+}). Overall, it appears the ISX treatment is effective for the $Cu(NH_3)_4^{2+}$ complex in batch treatments or in continuous flow operations using ISX as a filter precoat.

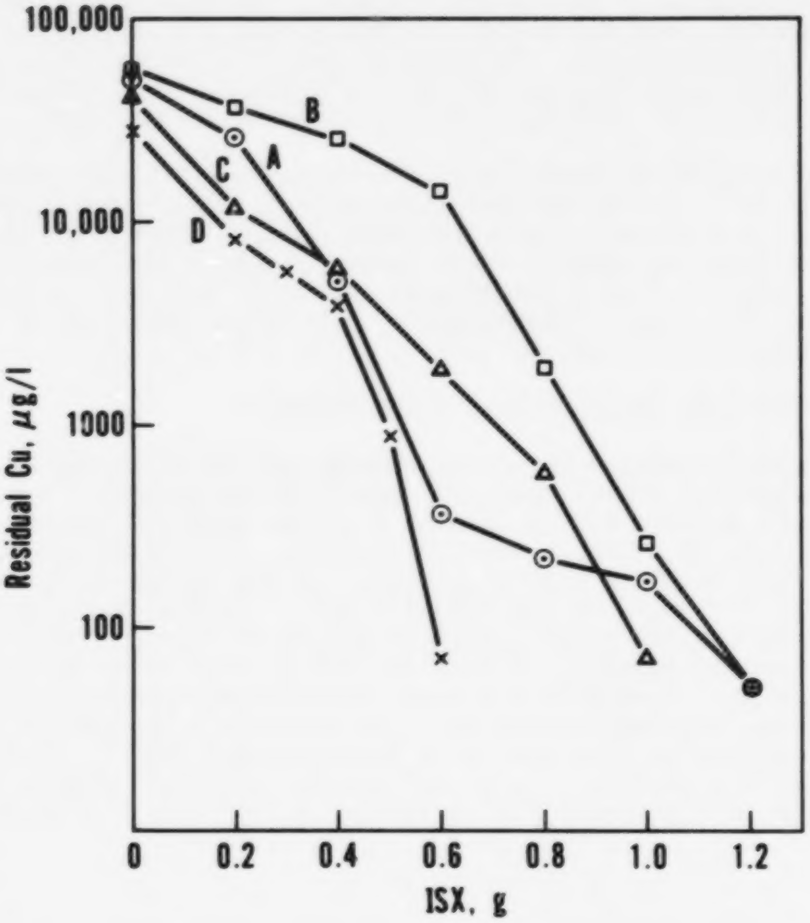

Figure 20. Copper ammonia complex removal with ISX.

Copper ammonia complex solutions (1,000 ml) were treated with increasing amounts of ISX (capacity = 1.5 meq metal ion/g). Aliquots (10 ml) of the supernatant were removed for copper analysis 5 min after each addition. Theoretical weight required is 1.02 g for the 50 mg/1 copper ammonia solution.

Curve A. $Cu(NH_3)_4^{2+}$ standard solution (50 mg/1 as Cu-initial); theoretical weight ISX required is 1.02 g.

Curve B. $Cu(NH_3)_4^{2+}$ commercial rinse (53.63 mg/1 Cu-initial); theoretical weight ISX required is 1.09 g.

Curve C. $Cu(NH_3)_4^{2+}$ commercial rinse (41.77 mg/1 Cu-initial); theoretical weight ISX required is 0.85 g.

Curve D. $Cu(NH_3)_4^{2+}$ commercial rinse (28.35 mg/1 Cu-initial); theoretical weight ISX required is 0.58 g.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The Northern Regional Research Center developed an effective process to remove heavy metals from wastewaters of two nonferrous metal industries and insoluble starch xanthate (ISX). The study included bench-scale evaluation of wastewaters from two lead battery and one brass mill waste. The evaluation included: (1) Determination of the metals and concentrations in the raw and treated wastewaters; (2) treatment with ISX alone and in combination with selected coagulant aids; (3) recovery of heavy metals from ISX sludge; and (4) determination of the potential reuse of the treated effluent. Several other effective and economical treatment processes were also developed for specific waste streams from printed circuit manufacturers. Based on the evaluation of results in this study, recommendations were made as to the desirability of constructing a prototype plant for actual on-site testing in selected industries. This report contains an extensive bibliography of references dealing with these industries.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Control Water Pollution Toxic Metal Control Industrial Wastes Metal Finishing	Insoluble Starch Xanthate Copper Removal from Rinse Waters Brass Mill Wastewaters Lead Battery Effluents	68D

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